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# *Organic Analytical Reagents*

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VOLUME FOUR

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BY

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**TO MY FATHER**

whose clear vision and deep understanding have contributed so much to the preparation of this work.



## PREFACE

Since the earliest days of analytical chemistry, organic reagents have been employed in various ways to facilitate the detection and determination of chemical substances. Only during the past two or three decades, however, have these compounds been used extensively in analytical procedures. At present they are rapidly gaining in popularity because of their greater sensitivity and specificity as compared to inorganic reagents, and also because of the greater convenience with which they may be employed in many analytical procedures.

The principal purpose in preparing this book has been to assemble in one place a description of all organic compounds used in the analysis of inorganic substances, and to present a discussion of the methods employing these reagents.

The information used in this book is taken from all publications appearing prior to January 1, 1946. Due to conditions resulting from the war, foreign journals have been delayed or prevented from reaching the United States, and in consequence much of the material contained in the more recent publications has been taken from *Chemical Abstracts*. For this reason, not all articles published before January 1, 1946, have been reviewed. The chemist who uses this book in reviewing the literature may, however, be guided by this principle: that all articles appearing in *Chemical Abstracts* up to and including 1945, as well as all original journals available to this date, have been included.

References to the literature have been made so as to indicate, at least to some extent, the subject matter of each. Thus the chemist who wishes to use a certain reagent for a given purpose has available a comment on almost every article that has been written on the subject and, in addition, the reference to the original publication in the event he wishes to consult this source. In this connection, it may be helpful to note that bibliofilm or photostat copies of articles appearing in most chemical journals can be secured at moderate cost from the United States Department of Agriculture Library, Washington, D. C.

Many obviously inferior reagents and methods are included since the treatment of the subject is intended to be complete. The inclusion of inferior methods is justified because of two considerations: in the future no time need be lost in attempting analytical methods that in the past have been demonstrated as unsatisfactory; and further, an inferior method may, with suitable modifications, be made useful for certain purposes.

In order to promote a more comprehensive study and a wider use of organic compounds in inorganic analysis, methods have been included for the preparation of most compounds listed in the book. For most substances, several methods appear in the literature and, in selecting the one to be included, the author has been guided by the principle that it be the most adaptable in the average chemistry laboratory. It should be stated that only a few of the methods of synthesis described have been used by the author, and undoubtedly some may prove unsatisfactory. Consequently, any information regarding better methods is earnestly solicited.

The primary aim of this book has been to collect in one place all information relating to the analytical uses of a given compound, and this principle has been adhered to regardless of structural characteristics or analytical functions. In a classification based on functions alone, many compounds would necessarily appear in different sections. For example, benzidine is used as a reducing agent, a basic salinogenic compound and in diazotization and coupling reactions for nitrite. Further, any classifications based upon functional groups present in the organic molecule would be somewhat arbitrary, since many compounds possess more than one group which affects their chemical reactions. The plan finally adopted calls for the complete treatment of each compound in one section, since any disadvantage resulting from this lack of regard for function and structure is believed compensated by the convenience of localization of information. In general, chemically related compounds are grouped together in so far as this is practicable; thus, the alcohols, amines, acids, oximes, arsonic acids, etc., form separate sections. It must be emphasized that owing to the diverse character of the reagents used in analytical procedures the associations of these substances in separate sections of this book may be somewhat debatable from the purely chemical point of view, but the plan used here seemed to be the most practicable that could be devised by the author. Although this scheme may separate such substances as reducing agents or oxidizing agents through widely scattered parts of the book, every reference to a particular reagent will be found in the section devoted to that compound.

The author is painfully aware of the many inconsistencies and ambiguities which appear in various parts of this book. Contradictory claims made by various authors are purposely included in order that the analyst may properly evaluate their merit through additional research. Many vague descriptions of methods and procedures are presented simply because the original sources themselves are not clear. Frequently, too, in translations or in abstracts errors have been discovered, which indicates too clearly that many more must certainly have escaped notice. The possibility of any error, or incompleteness of description has not prevented inclusion of certain important material, since such omissions would lead to incomplete coverage of some topics. The author also realizes that he must accept the responsibility for many mistakes, and he earnestly hopes that these will be communicated to him.

Another source of error has appeared in many publications: due to the character of chemical nomenclature, often there has been some doubt as to exactly what compound is referred to in certain discussions. This is especially true of the dyes, but is true also of certain other compounds. Every effort has been made to see that these references have been properly evaluated.

*Indianapolis, Ind.*  
August, 1946

F. J. W.

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And finally, no thanks can adequately repay the patient self-denial of his wife and sons, who have spent altogether too many months without the companionship and associations which in normal times they have so much enjoyed.

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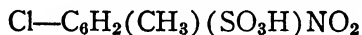


# CHAPTER I

## ACIDIC NITRO COMPOUNDS

A number of nitro compounds are useful in inorganic analysis because they form insoluble potassium salts. It has not been definitely established that the nitro group is in all cases responsible for the formation of potassium salts, but with some, such as dipicrylamine, the activity is explained only by the migration of a hydrogen atom to yield an hydroxy-acidic nitro group. It may not be safe to assume that all nitro compounds which yield insoluble potassium salts are acidic nitro compounds, especially since some contain phenolic groups, but for convenience in classification these compounds are included in this section.

### 6-CHLORO-5-NITROTOLUENE-3-SULFONIC ACID



**Use:** Detection of barium, potassium and rubidium.

Determination of potassium and rubidium.

This reagent is a colorless crystalline solid. It is soluble in water.

**Preparation:** *o-Toluidine-5-sulfonic acid:* Heat 165 g. of *o*-toluidine with 500 g. of concentrated sulfuric acid containing a trace of iodine for 6 hours at 160-165° C. Recrystallize the product from water.

*6-Chloro-m-toluene sulfonate:* Suspend 150 g. of *o*-toluidine-5-sulfonic acid in a mixture of 450 ml. of concentrated hydrochloric acid and 300 g. of powdered ice in a freezing mixture, and then diazotize with a concentrated solution containing 75 g. of 95 per cent sodium nitrite. Add the resulting diazo compound slowly to a cold solution containing 110 g. of cuprous chloride in 800 ml. of concentrated hydrochloric acid and 150 ml. of water. Heat on a water-bath for 90 minutes, and allow the mixture to stand overnight. Filter, wash the crystals with a little water and dry at 160° C. The yield may be increased by precipitating the copper as copper sulfide and then concentrating the diluted filtrate.

*Sodium-6-chloro-m-toluene sulfonyl chloride:* Treat the compound formed in the preceding step with phosphorus pentachloride according to the usual procedure for sulfonyl chloride formation.

*Nitration of 6-chloro-m-toluene sulfonyl chloride:* Add 100 g. of the sulfonyl chloride to a mixture of 75 ml. of nitric acid ( $d = 1.50$ ) and 150 ml. of sulfuric acid at 26° C. and stir. Carry out the nitration between 28° C. and 35° C. The reaction requires about 90 minutes for completion. Then pour the mixture into a large volume of ice water and collect the crystals. Wash with water and



dry under reduced pressure over phosphorus pentoxide. The melting point of the nitro compound is 41-46° C.

*Sodium salt of 6-chloro-5-nitrotoluene-3-sulfonic acid:* Boil 25.6 g. of the sulfonyl chloride under reflux for 5 hours with 50 ml. of 90 per cent alcohol, and evaporate the resulting red solution on a water-bath to a small volume. Dilute with water and again evaporate, and then repeat two more times. Titrate the solution with sodium hydroxide (about 3.9 g.), and evaporate the neutralized solution to dryness. Crystallize the yellow salt from water. The pure salt is colorless and is soluble in water.<sup>1,2</sup>

**Detection and determination of potassium.** Davies and Davies<sup>5</sup> observed that the potassium salt of 6-chloro-5-nitrotoluene-3-sulfonic acid is fairly insoluble in water, and suggested the use of this reagent for the detection and determination of potassium.<sup>3</sup> A solution of the sodium salt of 6-chloro-5-nitrotoluene-3-sulfonic acid yields a precipitate with a solution containing 1 part of potassium in 2500 parts of water. The potassium salt is sufficiently insoluble to be used for the quantitative determination of potassium, and the method is said to be at least as trustworthy as the chloroplatinate method, and in some instances may be even more convenient than the perchlorate method. The solubility of the potassium, ammonium and sodium salts of 6-chloro-5-nitrotoluene-3-sulfonic acid at different temperatures is given in Table 1.

TABLE 1.—SOLUBILITY OF ALKALI SALTS OF 6-CHLORO-5-NITRO-TOLUENE-3-SULFONIC ACID

(g. of salt per 100 g. of water)

Temp. ° C.	Potassium	Ammonium	Sodium
0	0.235	0.935	10.4
12.3	0.30	1.48	12.0
16.45	.....	.....	13.3
20.1	0.405	1.77	15.05
30.	0.57	2.58	20.0

The ammonium salt is sufficiently insoluble to interfere with the detection of potassium, and when present must be removed by boiling with sodium hydroxide. Potassium is then detected by adding 6-chloro-5-nitrotoluene-3-sulfonic acid to the cold alkaline solution. The potassium salt is moderately soluble in mineral acids. The aluminum and magnesium compounds are soluble and do not interfere. The barium and rubidium salts of 6-chloro-5-nitrotoluene-3-sulfonic acid are insoluble and may interfere. Frediani and Gamble<sup>4</sup> report that 6-chloro-5-nitrotoluene-3-sulfonic acid may be used for the microchemical detection of as little as 0.001γ of potassium, but that ammonium, barium, calcium, magnesium, strontium and lead salts interfere.

Davies and Davies<sup>5</sup> recommend 6-chloro-5-nitrotoluene-3-sulfonic acid for the determination of potassium. When only small quantities of potassium are to be determined, the most satisfactory results are obtained as follows: add the

weighed solid salt to a saturated solution of 6-chloro-5-nitrotoluene-3-sulfonic acid, dilute to the proper volume with water, boil until the solution is clear, and then allow to stand for 24 hours at ordinary temperatures. Collect the potassium salt on a Gooch crucible, allow to drain and slowly wash with 2-3 times its weight of water. Dry the precipitate to constant weight at 110° C.

Sulfate does not interfere in this determination as it does in the chloroplatinate and the perchlorate methods.<sup>6,7</sup> Moderate quantities of aluminum, sodium and magnesium do not appear to interfere, although the alkaline earth metals must be removed. The following procedure may be used for the determination of potassium.

**Reagent.** Prepare a saturated solution of the sodium salt of 6-chloro-5-nitrotoluene-3-sulfonic acid. The solution should be saturated at room temperature.

**Procedure.** To 15-25 ml. of a hot solution of a potassium salt containing 0.2-0.4 g. of potassium, add 25-40 ml. of the 6-chloro-5-nitrotoluene-3-sulfonic acid reagent. At least a 30 per cent excess of the theoretical quantity of the precipitant should be added. Boil the mixture gently for at least 5 minutes until the precipitate dissolves, adding more water if necessary. Allow the mixture to stand for 24 hours at ordinary temperature, and then filter on a Gooch crucible. Allow the precipitate to drain well, and slowly wash with 2-3 times its weight of water. Dry at 110° C. to constant weight. If the original solution contains considerable quantities of sodium or other metals, wash the precipitate with a few ml. of a saturated solution of the potassium salt of 6-chloro-5-nitrotoluene-3-sulfonic acid instead of water. The factor for potassium is 0.1350.

The results obtained in the analysis of a number of pure potassium salts, using the above method, are shown in Table 2.

TABLE 2.—DETERMINATION OF POTASSIUM IN PURE SALTS

Salt Used	Weight g.	Weight of Potassium Salt of Reagent		Per Cent of Potassium	
		Found	Theoretical	Found	Theoretical
KCl	0.5815	2.2391	2.260	51.9	52.31
KCl	0.8753	3.4033	3.401	52.35	52.31
KNaC <sub>4</sub> H <sub>4</sub> O <sub>6</sub> ·4H <sub>2</sub> O	1.1576	1.1942	1.189	13.87	13.83
KNaC <sub>4</sub> H <sub>4</sub> O <sub>6</sub> ·4H <sub>2</sub> O	1.1576	1.1940	1.189	13.87	13.83
KNaC <sub>4</sub> H <sub>4</sub> O <sub>6</sub> ·4H <sub>2</sub> O	1.1576	1.1938	1.189	13.87	13.83
KAl(SO <sub>4</sub> ) <sub>3</sub> ·12H <sub>2</sub> O	2.5271	1.5581	1.544	8.30	8.23
KCl	0.8753	3.3998	3.401	52.34	52.31
KCl	0.4377	1.7015	1.701	52.38	52.31
K <sub>2</sub> SO <sub>4</sub>	0.4515	1.5184	1.502	45.3	44.9

Dermer and Dermer<sup>8</sup> state that the solubility of the potassium salt of 6-chloro-5-nitrotoluene-3-sulfonic acid is too great to make the reagent a satis-

factory precipitant for potassium, and claim that attempts to decrease the solubility with non-aqueous solvents have not been promising. Further, various compounds in which fluorine, bromine or iodine have replaced the chlorine, or in which benzene has replaced toluene have been prepared and studied as possible precipitants for potassium. Only the 2-bromo-3-nitrotoluene-5-sulfonic acid is as satisfactory as the chlorine derivative. Its potassium salt is somewhat less soluble, but the ratio of solubility of the sodium salt to that of the potassium salt is not as favorable as 6-chloro-5-nitrotoluene-3-sulfonic acid.

**Determination of rubidium.** Like potassium, the rubidium salt of 6-chloro-5-nitrotoluene-3-sulfonic acid is only slightly soluble in water. This fact has been used by Benedetti-Pichler and Bryant<sup>9</sup> for the approximate determination of rubidium:

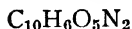
**Procedure.** Add to the rubidium solution an equal volume of a saturated solution of the sodium salt of 6-chloro-5-nitrotoluene-3-sulfonic acid. Mix well and cool in ice water for 10 minutes to precipitate the white crystalline rubidium salt. An approximate determination of rubidium may be obtained by comparing the volume of the precipitate with that obtained with standards similarly prepared.

**Detection of barium.** Rosenthaler<sup>10</sup> has found 6-chloro-5-nitrotoluene-3-sulfonic acid satisfactory for the microchemical detection of barium in the presence of calcium and strontium. Shrub-like, branched needles are obtained when a 5 per cent solution of the sodium salt of 6-chloro-5-nitrotoluene-3-sulfonic acid is added to a not too dilute solution of a barium salt. Calcium and strontium do not behave similarly, even in a 10 per cent solution, but these metals do interfere in great concentrations. In a pure solution, barium may be detected at a concentration of 1:2,000.

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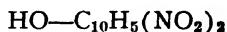
## 2,4-DINITRO-1-NAPHTHOL

Synonym: Martius yellow



Mol. Wt. 234.16

Beil. Ref. VI, 617.



**Use:** Detection of cobalt and thallium.

2,4-Dinitro-1-naphthol is obtained as yellow needles from alcohol. It melts at 138° C. It is almost insoluble in boiling water, but is slightly soluble in alcohol, ether and benzene. The sodium salt is known as Martins yellow.

**Preparation:** This compound is prepared by passing slowly a stream of the oxides of nitrogen, formed by the action of nitric acid on arsenious oxide and not dried, into an ice-cooled ether solution of  $\alpha$ -naphthol containing 10 g. of  $\alpha$ -naphthol in 100 ml. of ether. When the oxides of nitrogen are no longer absorbed (about 20 minutes), stop the flow of gas.<sup>1</sup>

**Detection of thallium.** A solution of 2,4-dinitro-1-naphthol in pyridine reacts with a solution of a thallium salt to give a precipitate of orange-yellow needles arranged in starlike clusters.<sup>2,3,4</sup>

**Reagent.** Prepare a saturated solution of 2,4-dinitro-1-naphthol in pyridine and dilute with three times as much water.

**Procedure.** Place a microdrop of thallium nitrate solution on an object glass, and add an equal sized drop of the reagent and stir quickly with a glass rod. The orange-yellow precipitate is observed under magnification. As little as 0.04% of thallium may be detected with this reagent at a limiting concentration of 1:100,000.

This test is recommended by Wenger and coworkers.<sup>5</sup>

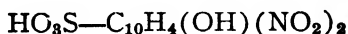
**Detection of cobalt.** Solutions of cobalt salts react with a pyridine solution of 2,4-dinitro- $\alpha$ -naphthol to yield pale orange-yellow rosettes.<sup>2,3</sup> The same reagent and procedure are employed as in making the test for thallium. The sensitivity of the cobalt reaction is 0.05%, and the limiting concentration is 1:10,000.

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## 1,5-DINITRO-2-NAPHTHOL-7-SULFONIC ACID

$C_{10}H_6O_8N_2S$

Mol. Wt. 314.21



**Use:** Detection of potassium and rubidium.

**Preparation:** 1,5-Dinitro-2-naphthol-7-sulfonic acid is prepared by the nitration of *F*-acid. Since technical *F*-acid contains some of the 2,6-isomer, it is necessary first to obtain a pure salt of *F*-acid. This is accomplished by converting to the barium salt and decomposing with sulfuric acid. The sodium salt of *F*-acid is obtained by neutralizing with sodium carbonate. The sodium salt of

*F*-acid is then nitrated with a mixture of nitric and sulfuric acids and the mixture is neutralized with calcium carbonate. Calcium sulfate is removed by filtration and the calcium salt obtained from the filtrate by evaporation.

**Detection of potassium and rubidium.** The potassium salt of 1,5-dinitro-2-naphthol-7-sulfonic acid,  $K[C_{10}H_4(OH)(NO_2)_2(SO_3)] \cdot H_2O$ , is obtained by treating a solution of a potassium salt with the calcium salt of the acid in neutral or slightly acid solution. The potassium compound is only very slightly soluble, and precipitation is made quantitative by the addition of ethyl alcohol. The precipitate does not form in an alkaline solution. Rubidium, lithium, ammonium, cupric, cobaltous, nickel and ferrous ions interfere when present even in very small quantities. Considerable quantities of zinc, magnesium, manganese, lead and oxalate also interfere, as does sodium if present in very large amounts.

Potassium may be determined after precipitation with 1,5-dinitro-2-naphthol-7-sulfonic acid by treating with concentrated sulfuric acid evaporating to dryness and weighing as potassium sulfate. Upon treating a solution of the potassium salt of 1,5-dinitro-2-naphthol-7-sulfonic acid with barium hydroxide, a salt,  $K_2Ba[C_{10}H_4O(NO_2)_2(SO_3)]_2$ , is obtained. This compound is red in color.

The rubidium salt of 1,5-dinitro-2-naphthol-7-sulfonic acid is less soluble than that of potassium, and it appears that 1,5-dinitro-2-naphthol-7-sulfonic acid may be useful for the detection and determination of rubidium.

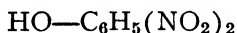
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## 2,4-DINITROPHENOL



Mol. Wt. 184.11

Beil. Ref. VI, 251.



**Use:** Detection of potassium, ammonium, magnesium, cesium, rubidium, and thallium.

2,4-Dinitrophenol consists of pale yellow rectangular plates. It melts at 114° C., and may be sublimed in small quantities without decomposition. It is soluble in ether and hot water, but is somewhat less soluble in hot alcohol.

**Preparation:** Mix 20 g. of chlorobenzene with 30.5 ml. of concentrated sulfuric acid in a round flask, and warm on a water-bath with mechanical stirring. Mix 40 ml. of nitric acid with 30.5 ml. of concentrated sulfuric acid and add this mixture to the chlorobenzene solution at such rate that the temperature remains below 100° C. When all the acid has been added, stir the mixture for an hour on a water-bath and heat to boiling, and then heat for another hour at 120° C. in an oil-bath. Pour the liquid onto crushed ice and water and stir. Filter off the solid nitro compound, wash well with cold water and press down. Dry on a porous plate.

Mix 25 g. of the crude dinitrochlorobenzene obtained above with 13 g. of sodium hydroxide in 500 ml. of water and boil in a round flask for about 90

minutes, or until the liquid is clear. Filter hot, and acidify with hydrochloric acid. Allow to cool, and filter off the precipitate of 2,4-dinitrophenol. Wash with water and dry on a porous plate. Purify by recrystallizing from hot water.<sup>1,2</sup>

**Detection of potassium, ammonium and magnesium salts.** When a saturated solution of the reagent in 2 per cent aqueous sodium carbonate is added to a solution containing potassium salts, broad, yellow, rectangular plates separate, which appear greenish-yellow under crossed Nichols. By means of this reaction 13γ of potassium can be detected microscopically. Ammonium, arsenate, arsenite, lithium and sodium ions do not precipitate on the addition of the reagent to solutions containing 10 mg. of the ion per ml. Cesium, rubidium and thallous salts yield precipitates similar to those with potassium, the first being the most soluble. Antimony, bismuth, cadmium, stannous and stannic tin form white amorphous precipitates, followed by the appearance of irregular colorless crystals. The reagent cannot be used with aluminum, barium, calcium, cobalt, chromium, copper, iron, lead, magnesium, manganese, mercury, nickel, silver, strontium and zinc.<sup>3,4</sup>

Rosenthaler<sup>4</sup> also reports that 2,4-dinitrophenol yields characteristic crystals with ammonium and magnesium salts, but these reactions appear to be of doubtful analytical value.

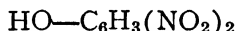
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2. Engelhardt and Latschinow, *Zeit. f. Chemie.* 233 (1870).
3. H. A. Frediani and L. Gamble, *Mikrochem. ver. Mikrochim. Acta.* **29**, 22 (1941).
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## 2,6-DINITROPHENOL



Mol. Wt. 184.11

Beil. Ref. VI, 257.



**Use:** Detection of ammonium, potassium and sodium.

2,6-Dinitrophenol is obtained as light yellow, fine needles by crystallizing from water. It melts at 61.8° C. It dissolves in water, and is readily soluble in benzene, chloroform, ether and boiling alcohol.

**Preparation:** 2,6-Dinitrophenol is prepared by the nitration of *o*-nitrophenol.<sup>1,2</sup>

**Detection of potassium, sodium and ammonium.** Rosenthaler<sup>3</sup> has proposed the use of 2,6-dinitrophenol as a microchemical reagent for the detection of potassium, ammonium and sodium. The reagent is a saturated solution of the nitrophenol in 2 per cent sodium carbonate. The potassium salt forms as deep orange-colored crystals, and the ammonium salt as bright yellow crystals. Frediani and Gamble,<sup>4</sup> who have investigated the many reagents which have been proposed for the detection of potassium, claim that the potassium salts of 2,6-dinitrophenol are formed only under conditions which are too exacting to meet the requirements of an analytical procedure.

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**DIPICRYLAMINE**

Synonym: Hexanitrodiphenylamine, aurantia

 $C_{12}H_5O_{12}N_7$ 

Mol. Wt. 439.22

Beil. Ref. XII, 766(369).



**Use:** Detection and determination of beryllium, cesium, lead, mercury, potassium, rubidium, thallium and zirconium.

Dipicrylamine is obtained as a light yellow crystalline solid by crystallizing from acetic acid. It melts at 244-246° C. with decomposition. It is almost insoluble in water and ether, but dissolves readily in glacial acetic acid. Aurantia, which is the ammonium salt of dipicrylamine, is obtained as a reddish-brown crystalline solid.

**Preparation:** Dissolve diphenylamine in concentrated sulfuric acid and carefully pour this solution into fuming nitric acid. After the first violent reaction has subsided, the mixture is warmed gently for a time to complete the nitration. Pour the mixture into ice cold water and filter off the yellow crystalline solid. Wash until free from acids and recrystallize from glacial acetic acid.<sup>1,2,3</sup>

Hoffman and Dame<sup>36</sup> have described the following method, using chlorobenzene:

**Preparation: Dinitrochlorobenzene:** Add gradually over a period of 2 hours 101.7 g. of chlorobenzene to 507 g. of a mixture consisting of 67.26 per cent sulfuric acid, 30.06 per cent nitric acid, 0.16 per cent nitrous acid, and 2.52 per cent water. Heat slowly to 95° C., and keep at this temperature for 2 hours. A light yellow liquid separates and solidifies on cooling. Drain off the acid mixture, add water to the solid, and break up the mass under water. Filter, and repeat the treatment with water several times. Then wash several times while molten under hot water. Again treat with cold water, crush, filter, and dry. An additional quantity of this product is obtained by pouring the spent acid into a large volume of water, filtering, washing, and drying.

**Dinitrodiphenylamine:** Add 150 g. of the above material to approximately 137.7 g. of aniline, and stir the mixture 2 hours at 18-29° C. Pour the resulting mass into cold water, filter, and wash several times with dilute hydrochloric acid, and then with water. Dry at 75-100° C.

**Tetranitrodiphenylamine:** Heat 840 g. of nitric acid (d. 1.33) to 40° C. in a large beaker, and to this add 100 g. of the dinitrodiphenylamine in small portions with mixing, while keeping the temperature at 50-60° C. Cool, filter, wash free of acid, and dry.

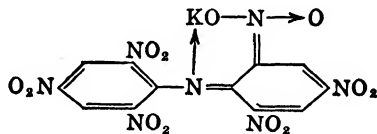
**Hexanitrodiphenylamine:** To 500 g. of a mixture consisting of 46 per cent sulfuric acid, 46.5 per cent nitric acid, and 7.5 per cent water at 20° C., add gradually over a period of 1 hour 50 g. of tetranitrodiphenylamine. Allow to

stand 4.5 hours at 32° C., and pour the mixture into a large volume of ice water. Filter off the yellow crystalline solid, wash free of acids, and recrystallize from glacial acetic acid.

**Detection of potassium.** Dipicrylamine dissolves in dilute sodium or ammonium hydroxide to form a strongly colored, orange-yellow solution. If a potassium salt is added to this solution, an orange-red, crystalline precipitate of potassium dipicrylamine is formed. This reaction may be used as a sensitive test for potassium.<sup>4-8,32,35</sup> The formation of the potassium salt has been explained as due to the replacement of the hydrogen atom of the imine group in the dipicrylamine molecule



but, it appears probable, that salt formation of dipicrylamine is due to replacement of the hydrogen atom of the hydroxyl group in the enol form to give a compound having the following composition:



Poluektov<sup>4,5</sup> has used the ammonium salt of dipicrylamine (aurantia) as a reagent in a spot test for detecting potassium.

**Procedure.** Dissolve 0.2 g. of aurantia in 2 ml. of N sodium carbonate solution and 20 ml. of water and heat to boiling. Place 1 drop of the solution to be tested on a strip of filter paper, and immediately add a drop of the reagent solution. An orange-red spot is formed if potassium is present. By means of this reaction 0.003 mg. of potassium can be detected.

Feigl and Barbosa<sup>6,35</sup> recommend a procedure using the sodium salt of dipicrylamine instead of aurantia as the reagent.

**Procedure.** Dissolve 0.2 g. of sodium dipicrylamine in 2 ml. of 2 N sodium carbonate and dilute with water to 15 ml. Filter. Soak filter paper (Schleicher and Schull No. 598) in this solution, and dry in a current of hot air. This reagent is stable for several months when stored in dry containers. A strip of the test paper when immersed in a solution containing potassium ions is colored red to rose, depending upon the concentration of the potassium salt. By means of this reaction 3γ of potassium can be detected in 1 drop of solution. By means of a spot plate procedure, only 12γ of potassium can be detected. In the absence of potassium, and in acid solution, the paper turns yellow, due to the formation of free dipicrylamine.

The presence of zinc diminishes the sensitivity of this reaction, probably due to the hydrolysis of the reagent. The reaction is characteristic of potassium in the presence of the alkali and alkaline earth metals, excepting rubidium and cesium. Large quantities of ammonium salts also give a precipitate, and should



therefore be removed by heating the solid to be analyzed to redness before making the final test. To detect potassium in the presence of other metals, evaporate the solution to dryness, treat the residue with an alkali, and apply the test to the filtrate obtained from this mixture.

**Microchemical reactions.** The formation of crystalline compounds of dipicrylamine with potassium, rubidium, cesium and other metals may be used for the microchemical detection of these elements.<sup>9-10,33</sup> A 2 per cent aqueous solution of dipicrylamine gives characteristic microcrystals with solutions of potassium salts which are not less than 0.012 N. The ammonium ion interferes with this reaction, but sodium, lithium, magnesium, barium, strontium, and calcium are without effect. Amorphous precipitates are obtained with aluminum, ferric, chromic, mercurous, nickel, cobalt and bismuth salts. Cesium, rubidium, lead and mercuric ions also yield crystalline precipitates with dipicrylamine, and can be used for the microchemical detection of these elements. The limiting concentrations of these ions which give a reaction with dipicrylamine is given in Table 3.

TABLE 3.

Ion	Concentration
Cesium .....	0.0005 N
Rubidium .....	0.0015 N
Lead .....	0.0015 N
Mercuric .....	0.002 N

According to Sheintsis,<sup>9,14</sup> the sodium salt of dipicrylamine reacts with potassium, cesium, rubidium, thallium, beryllium, zirconium, lead and mercuric ions to yield characteristically shaped and colored crystals, although Shapiro<sup>15</sup> claims that many of these precipitates are precipitates of the reagent. Sheintsis<sup>9</sup> has shown that zirconium, beryllium, ferric, chromic, aluminum, nickel, cobalt, copper and mercury ions yield salts with dipicrylamine which are soluble in ether, and leave behind oxides when ignited in a crucible.

A saturated solution of the sodium salt of dipicrylamine in a mixture of ethyl alcohol and water yields an orange-yellow precipitate of varying crystalline form with thallium. The sensitivity of this reaction is 1 $\gamma$  at a limiting concentration of 1:10,000. As little as 0.01 $\gamma$  of beryllium, at a limiting concentration of 1:1,000,000, may be detected by means of the yellowish crystals which are formed when an alcohol-water solution of the sodium salt of dipicrylamine is added to a solution of a beryllium salt.<sup>13</sup>

Sheintsis<sup>12</sup> recommends the use of the magnesium salt of dipicrylamine as a more satisfactory reagent than the sodium salt for the microchemical detection of potassium, rubidium, cesium, thallium, lead and mercuric ions.

**Gravimetric determination of potassium, cesium and rubidium.** The precipitate formed when dipicrylamine is added to a solution of potassium salt is sufficiently insoluble in cold water to be used for the gravimetric determination

of potassium,<sup>17-19</sup> and for the separation of potassium from sodium and the alkaline earth metals.<sup>20-22</sup> At 0° C. the solubility of potassium dipicrylamine is only 0.073 g. per liter of water, while at 25° C. the solubility is increased to 0.88 g. per liter. The precipitate of potassium dipicrylamine contains 8.194 per cent potassium. Kolthoff and Bendix<sup>19</sup> report that results accurate to within less than 2 per cent can be obtained with as little as 1 mg. of potassium.

Several salts of dipicrylamine have been recommended for the determination of potassium, rubidium and cesium, but the best results appear to have been obtained with the magnesium salt.<sup>17,18</sup> With this reagent it is possible to determine 0.2-0.4 mg. of potassium within approximately 0.5 per cent of the true value, even in the presence of as much as 8 mg. of sodium. The magnesium reagent is not suitable when phosphate is present, and the sodium salt is then substituted. It is necessary to use at least a 50 per cent excess of the reagent, and to carry out the precipitation in a hot solution, and then allow the salt to crystallize for a period of 12 hours. Dworzak and Ballczo<sup>18</sup> recommend washing the precipitate, first with the filtrate, and then with ether, in which the reagent is soluble, but in which the potassium salt does not dissolve. The following procedure for determining potassium, rubidium or cesium is recommended by Sheintsis.<sup>17</sup>

**Reagent.** Mix 12 g. of dipicrylamine with 5 g. of magnesium oxide and place the mixture in a 500-ml. Erlenmeyer flask with 400 ml. of water. Stir well and allow to stand for 15-20 hours and filter. The filtrate is a 3 per cent solution of the magnesium salt.

**Procedure.** Add rapidly a 25-50 per cent excess of the 3 per cent solution of magnesium dipicrylamine, with constant stirring, to the solution to be analyzed. Allow the mixture to settle for 30 minutes if not less than 10 mg. of the cation is present, but if small quantities are present, allow the mixture to stand for 2 hours. Filter, wash with anhydrous ether cooled to 10° C., dry the precipitate at 80-90° C. and weigh. The factor for potassium is 0.08194.

Results obtained by this method are satisfactory for potassium, rubidium and cesium with quantities of these elements ranging from 0.2-0.005 g. Barium is markedly coprecipitated.

The following method is described by Kolthoff and Bendix.<sup>19</sup>

**Procedure.** Weigh together an ordinary 30 ml. porcelain crucible containing a thin glass stirring rod and a small Emich porcelain filter stick. Weigh the material to be analyzed and place in the crucible, and dissolve in a sufficient volume of water so that the sample contains 2 mg. of potassium per ml. If the solution is acid, neutralize with sodium hydroxide until neutral to thymol blue; if alkaline, neutralize with hydrochloric acid, using the same indicator. Add dropwise with constant stirring, a 50-100 per cent excess of 3 per cent magnesium dipicrylamine reagent (7 ml. for 10 mg. of potassium). Place the crucible, stirring rod and filter stick in ice water for 15 minutes and then mount the filter stick just above the bottom of the dish and remove the supernatant liquid. Suck the precipitate dry and wash once with 1 ml. of ice water, and then with 3 or 4, 1-ml. portions of a saturated solution of potassium dipicrylamine

in ice water, and finally with 0.5 ml. of ice water. Disconnect the filter stick and place in the crucible with the stirring rod. Wipe the outside of the crucible clean and dry at 110° C. for 1 hour. Cool in a desiccator and weigh. The weight of potassium in the precipitate is calculated from the factor 0.08194.

Results obtained using dipicrylamine for the determination of potassium in the presence of other metals is given in Table 4.

TABLE 4.—GRAVIMETRIC DETERMINATION OF POTASSIUM WITH DIPICRYLAMINE

K added mg.	Cation Present	Amt. of Ca-tion Added mg.	Wt. of K Dipicryl-amine mg.	K Found mg.	Rel. Error Per Cent
10	.....	...	0.1215	9.95	—0.5
10	.....	...	0.1217	9.97	—0.3
10	.....	...	0.1220	9.99	—0.1
10	Lithium	12	0.1218	9.98	—0.2
10	Lithium	50	0.1235	10.12	+1.2
10	Lithium	109	0.1261	10.33	+3.3
10	Magnesium	10	0.1219	9.99	—0.1
10	Magnesium	50	0.1219	9.99	—0.1
10	Magnesium	100	0.1217	9.97	—0.3
10	Magnesium	200	0.1230	10.08	+0.8
10	Calcium	32	0.1221	10.00	0.0
10	Calcium	84	0.1226	10.04	+0.4
10	Calcium	170	0.1230	10.08	+0.8
10	Calcium	320	0.1284	10.52	+5.2
10	Barium	6	0.1293	10.60	+6.0
10	Barium	27	0.1606	13.20	+32.0
10	Barium	52	0.1961	16.10	+61.0

*Titrimetric determination of potassium:* Winkel and Maas<sup>23</sup> have reported a rapid titrimetric method for the determination of potassium after precipitating with dipicrylamine. The precipitate is dissolved in acetone, the solution diluted with water to an acetone concentration of 20-30 per cent and the resulting mixture titrated conductometrically with 0.1 N hydrochloric acid. This method permits the determination of 1.7 mg. of K<sub>2</sub>O in 5 ml. of solution within 0.5 per cent of the correct value.<sup>24</sup>

A somewhat different method is based upon treating the acetone solution of potassium dipicrylamine with a measured volume of standard hydrochloric acid, boiling to remove carbon dioxide and acetone, filtering, and then titrating the excess acid with standard sodium hydroxide solution in the presence of bromthymol blue.<sup>19</sup>

Portnov and Afanas'ev<sup>25</sup> have proposed a titrimetric procedure which depends upon treating a solution of the potassium salt with a measured excess of a standard solution of magnesium dipicrylamine, filtering off the potassium salt, and titrating the excess reagent in the filtrate with 0.1 N hydrochloric acid.

**Procedure.** Treat 0.2-0.8 g. of the sample, depending upon its potassium content, with 20-50 ml. of a standard solution of the magnesium salt of dipicrylamine. Dilute to a definite volume (50-100 ml.), filter from the potassium salt, and titrate an aliquot of the filtrate with 0.1 N hydrochloric acid potentiometrically or conductometrically. One ml. of 0.1 N acid corresponds to 3.91 mg. of potassium.

The results obtained in this method are accurate to 0.5-1.5 per cent. The quantity of acid used in titrating the potassium salt of dipicrylamine is equivalent to the amount of potassium in the precipitate.

When acid is added to an acetone solution of potassium dipicrylamine, the amine precipitates and the solution changes in color from red to yellow. According to Sueda and Kaneko,<sup>26</sup> it is necessary only to measure the volume of acid required to cause the disappearance of the reddish color instead of using another indicator. Further, by this method it is not necessary to filter the solution, but the method is not satisfactory in the presence of too much acetone. The color changes from yellow to red are much sharper than those from red to yellow, and consequently better results are obtained by adding an excess of the acid and back-titrating with a standard base.

Sheintsis<sup>27</sup> has based a titrimetric procedure for the determination of potassium, cesium and rubidium upon the reduction of the six nitro groups in the potassium, cesium and rubidium precipitates by means of a measured excess of trivalent titanium or divalent vanadium and titrating the excess of these ions with standard ferric ammonium sulfate solution.

**Procedure.** Place the sample to be analyzed in a centrifuge tube and add a 2.5 per cent solution of magnesium dipicrylamine until the liquid formed above the precipitate is dark red in color (color of the reagent). Allow the mixture to stand for 5-10 minutes and centrifuge for 5-10 minutes at 2000-3000 r.p.m. Wash the precipitate with a saturated solution of magnesium sulfate at 0° C. until colorless, each time separating the wash liquid from the precipitate with the aid of the centrifuge. Dissolve the precipitate in a 50 per cent water-acetone mixture and dilute the resulting solution with 50 per cent water-acetone mixture to a volume such that 1 ml. of the resulting solution contains not more than 0.01 mg. of potassium. Place a 10- to 20-fold, carefully weighed excess of  $\text{Ti}_2(\text{SO}_4)_3$  in a 25- or a 50-ml. flask containing carbon dioxide, and then add an aliquot of the above solution. Pass a stream of carbon dioxide into the flask for 5 minutes, and titrate the excess titanium with ferric ammonium sulfate solution, using a 10 per cent ammonium thiocyanate solution or leucomethylene blue as an indicator. If ammonium thiocyanate is used as the indicator, acidify the mixture with 5 ml. of 1:4 sulfuric acid, add 2 ml. of the indicator and titrate to the appearance of a slightly brownish-red color. If leucomethylene blue is used, add 2 ml. of the indicator and titrate to the appearance of a slightly bright green color. This method is accurate for 0.1-10 mg. of potassium.

Kiba<sup>28</sup> recommends titrating the precipitates of potassium, cesium and rubidium dipicrylamines with a standard solution of trivalent titanium, and determining the end-point potentiometrically.

The following procedure is used when bivalent vanadium is employed as the titrating agent.<sup>29</sup>

**Procedure.** Add a solution of magnesium dipicrylamine to the solution to be analyzed until the liquid above the precipitate is colored. The reagent should be added rapidly with constant stirring. Allow the mixture to stand for 5-30 minutes, centrifuge, and wash the precipitate with anhydrous ether until the residue becomes solid and does not adhere to walls of tube. Dissolve the precipitate in acetone and use an aliquot part for analysis.

Transfer the solution to an Erlenmeyer flask into which a stream of carbon dioxide is passed, and then add 5-6 times as much standard vanadium solution as is required to reduce the dipicrylamine. Allow the mixture to stand for 5 minutes with constant introduction of carbon dioxide. Titrate the excess  $V^{++}$  with ferric ammonium sulfate solution, using safranin as an indicator.

**Colorimetric determination of potassium.** Kolthoff and Bendix<sup>19</sup> recommend the use of a colorimetric method for determining microquantities of potassium. Aqueous solutions of potassium dipicrylamine vary in color from orange-red for saturated solutions to light yellow with low concentrations. Beer's law does not apply to these solutions, and consequently a colorimeter cannot be used. The determination may be made by means of a photoelectric colorimeter and a calibration curve by comparing with standards, or by means of a colorimetric titration. Since aqueous solutions of potassium dipicrylamine undergo hydrolysis, 1 ml. of 0.1 N sodium hydroxide is added to every 100 ml. of the solution to be analyzed to repress hydrolysis. The following procedure is used:

**Reagent.** Mix 12 g. of dipicrylamine with 5 g. of magnesium oxide and transfer the mixture to a 500-ml. Erlenmeyer flask with 400 ml. of water. Stir well and allow to stand 15-20 hours and filter.

The sodium salt of dipicrylamine may be used for the colorimetric determination, and this solution is prepared by mixing dipicrylamine with a slight excess of sodium carbonate and diluting the resulting mixture with water to give a solution which contains 3 per cent of the dipicrylamine.

**Procedure.** Evaporate the solution to dryness in a 20-ml. porcelain crucible, and add 3 drops of either the sodium or magnesium reagent. Place the crucible in ice water for 15 minutes, and without removing the crucible from the ice water, collect the precipitate on a filter stick which has been cooled in ice water. Remove the mother liquid by suction, and wash the precipitate with 2 drops of ice water, and then with 7-10 drops of a saturated solution of potassium dipicrylamine in ice water, and finally with 1 drop of ice water. Remove the filter stick from the suction tube, and fill the longer section of the stick (Figure 1) with acetone by means of a small pipet. The end opposite the asbestos plug is placed in the mouth, and the acetone is blown through the asbestos and the solution is collected in the crucible in which the precipitation was originally carried out. This procedure is repeated until all the precipitate is dissolved and the acetone comes through colorless. Dilute the acetone solution to 100 ml. with water containing 1 ml. of 0.1 N sodium hydroxide per 100 ml. Match the

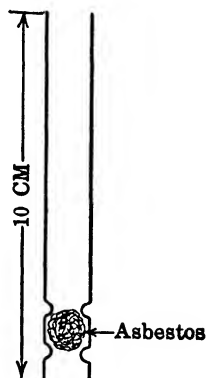


FIG. 1.

colors in a Nessler tube, or measure with a photoelectric colorimeter for which a calibration curve has been prepared. The results obtained using the colorimetric method for determining potassium in the presence of other ions is given in Table 5.

TABLE 5.—COLORIMETRIC DETERMINATION OF POTASSIUM IN THE PRESENCE OF FOREIGN IONS

Foreign Ion	Amount of Foreign Ion mg.	Potassium Taken $\gamma$	Potassium Found $\gamma$	Error $\gamma$
.....	...	50	47	-3
.....	...	50	48	-2
Sodium .....	0.5	50	48	-2
Sodium .....	1.0	50	45	-5
Sodium .....	3.0	50	48	-2
Magnesium .....	0.5	50	48	-2
Magnesium .....	1.0	50	50	0
Magnesium .....	3.0	50	54	+4
Lithium .....	1.0	50	50	0
Calcium .....	1.0	50	54	+4
Calcium .....	...	25	27	+2
Sodium .....	3.0	25	36	+11
Magnesium .....	1.0	25	29	+4
Lithium .....	1.0	25	29	+4
Calcium .....	1.0	25	29	+4

Amdur<sup>30,31</sup> has applied the colorimetric principle to the determination of small quantities of potassium in tissues and blood. An indirect empirical method has been developed for which the authors claim certain advantages over the procedure of Kolthoff and Bendix. It is more rapid, requires less manipulation and apparatus, uses less reagent per determination, and is capable of more accurate results.

**Reagent.** *Lithium dipicrylamine reagent:* Prepare a 0.6 per cent solution of lithium dipicrylamine as follows: Add 3 g. of dipicrylamine to a solution of 0.55 g. of lithium carbonate in 100 ml. of water. Heat to 50° C. and allow to stand for 24 hours, and then filter into a 500-ml. flask and dilute to about 500 ml. Again heat to 50 ml. and add moist potassium dipicrylamine until the solid no longer dissolves. The saturated solution is allowed to cool to room temperature, and is not filtered from the deposited crystals. The potassium salt used in the preparation of this reagent is formed by adding a few ml. of the 3 per cent lithium dipicrylamine solution to the calculated quantity of potassium chloride solution, followed by washing of the precipitate with distilled water.

*Standard potassium solution:* Prepare a solution of potassium sulfate or chloride which contains 0.1 mg. of potassium per ml.

**Procedure.** Arrange nine 15-ml. centrifuge tubes in a rack, and to the first add 1 ml. of the standard potassium solution, to the second add 2 ml. of the standard potassium solution, to the third, 3 ml., etc. Place the nine tubes in a drying oven and evaporate to dryness. Allow to cool to room temperature and add 1 ml. of the freshly filtered reagent to each, using the same pipet. Mix the contents of the tubes by rotating between palms of the hands, and allow to stand for about 2 hours. Withdraw a 0.4-ml. sample from each, using a blood pipet, the tip of which is covered by a small piece of filter paper held in place by a rubber band. Remove the filter paper and dilute to the mark, and then rinse the contents into a 100-ml. volumetric flask and dilute to the mark with distilled water. The light transmission percentage is then determined and the values obtained for the nine standard samples and for 0.4 ml. of the reagent diluted to 100 ml. are plotted to give a standard curve, such as that shown in Figure 2.

The unknown is then determined by exactly the same treatment, using the same pipet which was used in preparing the standard curve, and comparing the observed transmission percentage with it.

The most exact determinations are made with samples containing from 0.3-0.8 mg. of potassium.

The reproducibility of results using this method appear to depend almost entirely upon the reproducibility with which the chemical procedure is carried out. It is important therefore for the highest accuracy that the same pipets should be used for both standards and unknowns, and if a 1-ml. delivering pipet is used, a reproducible drainage procedure is imperative.

Samples containing less than 0.15 mg. of potassium may be determined by plotting a curve with a more dilute reagent, or by adding 0.15 mg. of potassium to each sample. The latter procedure appears to be the more satisfactory, since the use of more dilute solutions lengthens the time necessary for complete precipitation, and also renders the determination more sensitive to temperature changes.

The lithium salt of dipicrylamine is used in this procedure because large quantities of magnesium or sodium may be present in the sample, and the use

of a magnesium or sodium reagent might increase the concentration of either ion to the point where appreciable coprecipitation takes place.

Köhn<sup>34</sup> has determined small quantities of potassium colorimetrically by measuring the fading of the color of a solution of magnesium dipicrylamine when the solution is used to precipitate potassium. The loss of color is proportional to the quantity of potassium precipitated.

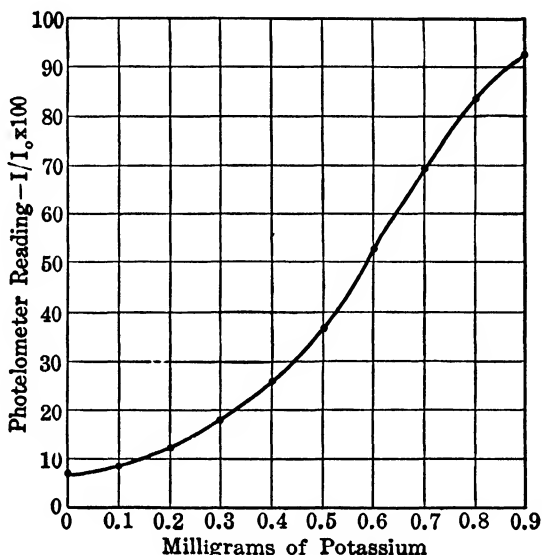


FIG. 2.

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## NAPHTHOL YELLOW S

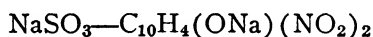
Synonym: 2,4-Dinitro-1-naphthol-7-sulfonic acid (sodium salt), citronin A, sulfur yellow S, acid yellow S

$C_{10}H_4O_8N_2SNa_2 \cdot 3H_2O$

Mol. Wt. 412.25

Beil. Ref. XI, 275(65).

Color Index, 10.



**Use:** Detection of cesium, hydrosulfites, mercury, potassium, rubidium, and tin.

Determination of potassium.

Naphthol yellow S is a light yellow or orange-yellow powder which dissolves in water to form a yellow solution. The free acid is known as flavianic acid.

**Preparation:** Add gradually 50 g. of  $\alpha$ -naphthol to 200 g. of 25 per cent fuming sulfuric acid and shake until solution is complete. Heat the mixture in an oil-bath at 125° C. for 1 hour. Remove a sample of the solution and mix with about 10 ml. of water in a test tube, and add 10 ml. of concentrated nitric acid and heat almost to boiling. If the yellow solution which is formed does not become turbid, nor flocks separate on cooling, the reaction is complete. Otherwise, add more concentrated oleum and continue heating until a sample shows the reaction to be complete.

Cool the melt and gradually mix with 500 g. of crushed ice. Filter and add 120 g. of nitric acid ( $d = 1.4$ ) to the brown filtrate, and heat for one-

half hour at 50° C. Allow the mixture to stand for 12 hours at room temperature and filter off the crystals which separate. Recrystallize from hot dilute hydrochloric acid and dry, first on a porous plate, and then in a desiccator over sulfuric acid or potassium hydroxide. The melting point is 151° C.<sup>1,2</sup>

**Detection and determination of potassium.** Clark and Willits<sup>3</sup> have proposed the use of naphthol yellow S for the detection of small quantities of potassium. A 2 per cent solution of the reagent added to 3½ times as much test solution is recommended for the procedure. This reagent will detect 1 part of potassium in 2500 parts of water. Considerable sodium does not interfere except by delaying the precipitation. This reagent is of particular interest for the potassium test since ammonium ions do not interfere. This is not true of the usual reagents such as chloroplatinic acid, perchloric acid, bismuth sulfate, tartaric acid, and sodium cobaltinitrite.

Naphthol yellow S is also suited to the microchemical detection of small quantities of potassium,<sup>4,5,6</sup> with which it forms characteristic crystals. The sensitivity of this reaction is 7.5 mg. of potassium per ml., and the limit of identification is 1.9γ when a saturated aqueous solution of the reagent is employed. Rubidium, barium, calcium, copper, lead, silver, strontium and thallous salts interfere, but aluminum, ammonium, antimony, arsenic, bismuth, cadmium, cesium, cobalt, chromium, iron, lithium, magnesium, manganese, mercury, nickel, sodium, zinc, and stannous salts do not. Free mineral acids prevent the formation of the precipitate, but acetic acid does not. Frediani<sup>4</sup> recommends that the reagent be crystallized 3 times from water and once from dilute hydrochloric acid before use. The melting point of the purified reagent is reported as 148-149.5° C.

Baranov<sup>7</sup> has used naphthol yellow S for the quantitative precipitation of potassium. He reports that this reagent is useful for determining potassium in fertilizers where no great accuracy is required.

**Detection of mercury.** Smith and Rogers<sup>8</sup> have reported a color reaction of naphthol yellow S with mercurous compounds:

**Procedure.** Place 5 ml. of the solution containing mercurous ion in a test tube and add 2 or 3 drops of an aqueous solution of naphthol yellow S and then add 1 N sulfuric acid until a precipitate is formed. A pink precipitate is obtained with mercurous salts.

**Detection of tin.** When 2 or 3 drops of a 2 per cent solution of naphthol yellow S are added to a solution of a stannous salt, and then sodium hydroxide is added dropwise, the color of the solution changes to bright red or pink. In the absence of other cations, this test is sensitive to 1 part of stannous tin in 2000 parts of water. In more dilute solutions, however, it is advisable to compare the color with that of a blank, since otherwise slight color changes may not be detected.<sup>9,10</sup> Silver, mercury, and bismuth compounds interfere with this test, since in the presence of the sodium stannite, formed in making the test, these ions are reduced to the metal. Most colored ions interfere, and with dilute solutions containing copper, an orange color may be observed. In the presence

of manganese the color is more violet, while with magnesium it exhibits an orchid tinge.

**Detection of rubidium and cesium.** In the absence of mercury, thallium tin, silver, lead and copper, rubidium can be detected in a neutral solution with the aid of a 0.5 per cent solution of naphthol yellow S in pure formic acid. In 1 drop of solution, rubidium can be detected by the formation of yellow acicular needles, which form if 3.0 mg. of rubidium is present in each ml. of solution.<sup>11</sup>

**Detection of hydrosulfitcs.** A red color appears if as little as 0.01 g. of sodium hydrosulfite is added to a solution of naphthol yellow S. In dilute or weakly alkaline solutions, the color is rose-pink. The color is fugitive, but persists for several minutes if ammonia is present.<sup>12</sup> The test is made as follows:

**Procedure.** Add an ammoniacal solution containing 0.02 per cent of naphthol yellow S to a few mg. of the substance to be tested or to 1 ml. of its solution. The rose color which develops with hydrosulfitcs is not given by most reducing agents.

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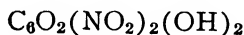
## NITRANILIC ACID

Synonym: 3,6-Dinitro-2,5-dihydroxyquinone



Mol. Wt. 230.09

Beil. Ref. VIII, 384.



**Use:** Detection of ammonium, barium, calcium, potassium and sodium.

Nitranilic acid is a golden-yellow, crystalline solid. It usually is obtained as the hydrate, but loses its water of hydration at 100° C., and explodes without melting at 170° C. It is readily soluble in water and alcohol, but is insoluble in ether. The aqueous solution of the compound decomposes on standing to form hydrogen cyanide and oxalic acid.

**Preparation:** *Hydroquinone diacetate:* Dissolve 1 mole of hydroquinone in a solution of 3 moles of sodium hydroxide in 100 ml. of water. Cool and mix with 500 g. of crushed ice, and add quickly 2.5 moles of acetic anhydride. Shake

the mixture vigorously for a few seconds, separate the crystalline product, and purify by crystallization.

**Nitranilic acid:** Dissolve one part of hydroquinonediacetate in 6 parts of fuming nitric acid ( $d = 1.48-1.5$ ) at about  $10^{\circ}\text{C}$ . Cool the mixture to  $-8^{\circ}\text{C}$ ., and pour into it 6 parts of concentrated sulfuric acid that has been cooled to  $-8^{\circ}\text{C}$ . Allow to stand for 1 hour at about  $0^{\circ}\text{C}$ ., and pour the mixture onto 12-15 parts of ice. Filter the precipitate quickly on a filtering cloth. Stir the precipitate with ice to form a paste and neutralize with potassium hydroxide. Allow the mixture to stand for 12 hours, and filter off the precipitate of potassium nitranilate and crystallize from hot water.

Add 10 g. of the finely powdered salt, which has been dried at  $150^{\circ}\text{C}$ ., to 40 ml. of ice cold nitric acid ( $d = 1.4$ ). Allow to stand for 1 hour and mix with an equal volume of ice water. Filter the precipitate with suction. Dissolve the free acid in the least possible quantity of water, and reprecipitate by adding one-third of its volume of concentrated nitric acid at  $0^{\circ}\text{C}$ .<sup>1</sup>

**Detection of sodium, potassium, ammonium, calcium, and barium.** Nitranilic acid reacts with solutions containing sodium, potassium, ammonium, calcium and barium salts to form characteristic crystals which may be used for the microdetection of these substances.<sup>2</sup>

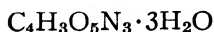
**Procedure.** To 4 ml. of the solution to be tested, add 1 ml. of glacial acetic acid, 25 ml. of ethyl alcohol, and 0.3-0.4 g. of nitranilic acid. Place the mixture in a refrigerator and examine after 24 hours for characteristic crystals.

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## 5-NITROBARBITURIC ACID

Synonym: Dilituric acid



Mol. Wt. 227.14

Beil. Ref. XXIV, 474(413).



**Use:** Detection and determination of potassium.

5-Nitrobarbituric acid is obtained as prisms and leaflets by crystallizing from water. It melts at  $181-183^{\circ}\text{C}$ . (when anhydrous) with decomposition. It is soluble in about 1200 parts of cold water, but is more soluble in hot water. It is insoluble in ether, but dissolves in alcohol and in solutions of sodium hydroxide.

**Preparation:** Place 143 ml. of fuming nitric acid ( $d = 1.52$ ) in a 2-liter flask. Fit the flask with a stirrer and immerse in a vessel filled with ice. While stirring, add 100 g. of barbituric acid over a period of 2 hours. The temperature should not rise above  $40^{\circ}\text{C}$ . during this period. Continue the stirring for 1 hour after all the barbituric acid has been added. Then add, while still stirring, 430 ml. of water with cooling to  $10^{\circ}\text{C}$ . Filter off the residue, wash and dry at  $60-80^{\circ}\text{C}$ . Dissolve the product in 860 ml. of boiling water, and pass steam through the mixture until solution is complete. Filter, and allow the filtrate to stand over-

night. Filter the crystals which form, wash with water, and dry in an oven at 90-95° C. for 2-3 hours.<sup>1,2</sup>

**Detection and determination of potassium.** 5-Nitrobarbituric acid reacts with solutions containing potassium ions to form a well-defined, stable, and difficultly soluble potassium salt. Precipitation may take place in an acid solution, since the reagent itself is strongly acid. This reaction may be used for the detection and determination of potassium. Precipitation is best carried out by using a 0.1 N 5-nitrobarbituric acid solution in 40 per cent alcohol. The potassium is precipitated from a chloride solution, which is either neutral or slightly acid. As little as 0.02 mg. of potassium per ml. of solution may be detected. Since the potassium salt of 5-nitrobarbituric acid consists of characteristic crystals, the formation of this compound may be used for the micro-detection of potassium.<sup>3,4,6</sup>

By using an acid solution of the reagent in making the potassium test, aluminum, antimony, arsenic, bismuth, chromium, iron, lithium, sodium and tin do not interfere.

Ammonium, rubidium, barium, cadmium, copper, manganese, calcium, cesium, cobalt, nickel, magnesium, zinc, strontium, mercury, silver, thallium and lead also form crystalline compounds, and interfere with the microdetection of potassium.<sup>5</sup>

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## NITROBENZENE

$C_6H_5NO_2$

Mol. Wt. 123.11

Beil. Ref. V, 233.

$C_6H_5NO_2$

**Use:** Detection of nitrate and sulfide.

Determination of chloride.

Nitrobenzene is a colorless to pale yellow, oily liquid, which has the odor of volatile almond oil. It has a sp. gr. of 1.205 and boils at 209° C. It dissolves in about 500 parts of water, but is freely soluble in alcohol, benzene and ether.

**Detection of nitrates and nitric acid.** Pesetz<sup>1-4</sup> has used nitrobenzene for the detection of nitrates and nitric acid. This test depends upon the formation of *m*-dinitrobenzene, and the conversion of this compound to a colored substance by the addition of acetone and sodium hydroxide.

**Procedure.** To a trace of a solid nitrate, add 10-12 drops of 1:10 solution of nitrobenzene in concentrated sulfuric acid, and heat on a steam-bath for 3 minutes. Then add 5-8 ml. of acetone and 3 ml. of a solution of sodium

hydroxide ( $d = 1.33$ ) diluted 3:1. A reddish color indicates the presence of nitrate. The test is sensitive to 0.1 mg. of nitrate.

The color obtained with nitrobenzene is more stable than that formed with benzene. If a nitrite, potassium bromide, or potassium iodide is present, the final sodium hydroxide phase is colorless.

**Determination of chlorides.** The principle objection to the determination of chlorides by the Volhard method lies in the necessity of removing the precipitated silver chloride. Since silver chloride is more soluble than silver thiocyanate, some of the silver chloride passes back into solution, thereby causing an error if not removed by filtration. The use of an immiscible liquid causes the precipitated silver chloride to accumulate at the interface of the two liquids, and thus removes it from the aqueous solution. Several liquids such as benzene and toluene have been recommended, but according to Caldwell and Moyer<sup>5</sup> nitrobenzene is the most suitable. Experiments indicate that in the presence of nitrobenzene no appreciable amount of silver chloride is carried down, and that nitrobenzene forms an insoluble layer over the precipitate so that the rate of solution of silver chloride is reduced to such an extent that it does not interfere with the final titration.

**Detection of sulfide.** Nitrobenzene reacts with sulfides in the presence of alcohol and sodium hydroxide to give a red coloration. This color appears only after a long time.<sup>6</sup>

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### $\alpha$ NITRO- $\beta$ -NAPHTHOL

$C_{10}H_7O_3N$

Mol. Wt. 189.16

Beil. Ref. VI, 653.

$HO-C_{10}H_6-NO_2$

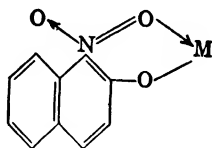
**Use:** Detection and determination of cobalt and palladium.

$\alpha$ -Nitro- $\beta$ -naphthol consists of yellow needles or leaves. It melts at 103° C. It is insoluble in water, but is soluble in alcohol, ether and glacial acetic acid.

**Preparation:** Shake pure yellow crystalline  $\alpha$ -nitroso- $\beta$ -naphthol with 10 times as much water by weight, and add an equal volume of nitric acid ( $d = 1.25$ ). Allow to stand for 1 hour, during which the color changes from yellow to gray. Filter, wash thoroughly with water, and treat with 30 parts of a solution prepared by diluting 1 part of 30 per cent sodium hydroxide with 50 parts of water. Filter and acidify the filtrate with acetic acid.  $\alpha$ -Nitro- $\beta$ -naphthol

separates as a bright yellow crystalline precipitate. Wash well and recrystallize 1 or 2 times from boiling alcohol.<sup>1</sup>

**Detection and determination of cobalt and palladium.** Herfeld and Gerngross<sup>2</sup> have reported that cobalt may be detected by precipitating with a solution of  $\alpha$ -nitroso- $\beta$ -naphthol. This reaction has been studied by Mayr<sup>3</sup> who reports that  $\alpha$ -nitro- $\beta$ -naphthol can replace  $\alpha$ -nitroso- $\beta$ -naphthol as a precipitant for cobalt and palladium. This reaction is interesting since the precipitates obtained with cobalt and palladium are similar to those formed with the nitroso-naphthols; consequently, the active group in the latter appears to be the hydroxyl group and not an oxime group obtained by enolization. The chelate compound formed probably has the following composition, in which  $M$  represents one equivalent of the metal:



Herfeld and Gerngross reported difficulty in obtaining a precipitate corresponding exactly to the formula of  $\text{Co}(\text{C}_{10}\text{H}_6\text{ONO}_2)_3$ , but according to Mayr this was due to the precipitation of the cobalt salt in the presence of hydrochloric acid. To obtain complete precipitation of cobalt, proceed as follows:

**Reagent.** Dissolve 2 g. of the solid reagent in 100 ml. of glacial acetic acid, dilute with 100 ml. of hot water, and filter. This solution keeps better than that of the corresponding nitroso compound.

**Procedure.** To 10-20 ml. of a solution containing a little mineral acid and 1-30 mg. of cobalt, add 10 drops of perhydrol, and sufficient sodium hydroxide to precipitate all the cobalt as  $\text{Co}(\text{OH})_3$ , avoiding an excess. Dissolve the precipitate by adding 10 ml. of glacial acetic acid, and dilute with hot water to 150-200 ml. Add about 50 per cent excess of  $\alpha$ -nitro- $\beta$ -naphthol, stir, and heat to boiling. Allow to settle and filter through a porcelain crucible. Wash 3 times with 30 per cent acetic acid and finally with water. Dry at  $130^\circ\text{C}$ . and weigh. The factor for cobalt is 0.09463.

Cobalt may be determined in the presence of a little iron by first removing the iron with cupferron. If much iron is present, as in the analysis of cobalt steel, remove iron, chromium, tungsten, molybdenum, titanium, copper and silicon by treatment with a suspension of zinc oxide at the boiling temperature. If nickel, zinc or manganese is present, it is necessary to precipitate cobalt from a solution containing more acetic acid.

Palladium can be precipitated by employing a procedure similar to that used for cobalt.

Recently Mayr and Proding<sup>4</sup> studied the precipitation of cobalt and palladium with  $\alpha$ -nitro- $\beta$ -naphthol and report that the perfectly pure nitro compound does not precipitate cobalt or palladium. The method generally employed for the precipitation of  $\alpha$ -nitro- $\beta$ -naphthol always results in the formation of

some  $\alpha$ -nitroso- $\beta$ -naphthol, and this is thought to be responsible for the precipitation of the metals.

The reaction with  $\alpha$ -nitro- $\beta$ -naphthol is recommended for the detection of cobalt. By using a solution of the sodium salt of the reagent, a sensitivity of 1:20,000,000 is claimed.

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2. H. Herfeld and O. Gerngross, *Z. anal. Chem.* **94**, 7-12 (1933); *C.A.* **27**, 5024 (1933).
3. C. Mayr, *Z. anal. Chem.* **98**, 402-8 (1934); *C.A.* **29**, 69 (1935).
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### ***o*-NITROPHENOL**

$C_6H_5O_3N$

Mol. Wt. 139.11

Beil. Ref. VI, 213.

$HO-C_6H_4-NO_2$

**Use:** Detection of ammonium and magnesium.

Determination of calcium.

*o*-Nitrophenol is a light yellow crystalline solid having a peculiar aromatic odor. It melts at 44-45° C. and boils at 214-216° C. It is volatile with steam. It is only slightly soluble in cold water but dissolves readily in hot water. It is also soluble in alcohol, benzene, ether, carbon disulfide and solutions of alkali hydroxides.

**Preparation:** Dissolve 80 g. of sodium nitrate or the equivalent of potassium nitrate in 200 ml. of water. Heat to facilitate solution, and to the still warm solution add 100 g. of concentrated sulfuric acid with stirring. Cool to 20° C. and add 50 g. of crystalline phenol which has been liquefied by warming with 5 ml. of water. Add the phenol solution dropwise from a separatory funnel with frequent shaking, and keep the temperature of the reaction mixture between 20° and 25° C. Allow to stand for 2 hours with frequent shaking, and then add 2 volumes of water. Allow to stand until the oil which separates has settled, and then carefully pour off as much as possible of the aqueous layer. Wash twice with water the oil which remains, and then distill the nitrophenol with steam. Filter with suction the *o*-nitrophenol from the aqueous distillate and dry on filter paper. Purify the crude product by again distilling with steam.<sup>1</sup>

**Detection of ammonium and magnesium.** Rosenthaler<sup>2</sup> has used a saturated aqueous solution of sodium *o*-nitrophenolate as a reagent for the microchemical detection of ammonium and magnesium. Characteristic crystals of the ammonium and magnesium salts are obtained.

**Determination of calcium.** Nitrophenol has been used by Jander and Hoffman<sup>3</sup> for the determination of calcium in a silicate mixture. Free calcium oxide is determined by the formation of calcium glycerate, which after separation from undecomposed silicates, is titrated with hydrochloric acid.



*o*-Nitrophenol in anhydrous methyl alcohol dissolves calcium oxide quantitatively from  $3\text{CaO} \cdot \text{SiO}_2$  and  $2\text{CaO} \cdot \text{SiO}_2$ . The resulting calcium *o*-nitrophenolate can be titrated with an alcoholic solution of hydrogen chloride. In the presence of  $3\text{CaO} \cdot 2\text{SiO}_2$ , the  $3\text{CaO} \cdot \text{SiO}_2$  and  $2\text{CaO} \cdot \text{SiO}_2$  are determined by the following process: Mix the finely powdered silicate mixture with 25 ml. of a 0.5 per cent solution of *o*-nitrophenol in anhydrous methyl alcohol and then heat to boiling with frequent shaking. After filtering from the undecomposed silicate, titrate the calcium nitrophenolate with a solution of hydrogen chloride in anhydrous methyl alcohol until the color changes from orange to yellow. Repeat until upon heating no further orange color appears. Standardize the alcoholic hydrogen chloride solution against calcium oxide.

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### *p*-NITROPHENOL

$\text{C}_6\text{H}_5\text{O}_3\text{N}$

Mol. Wt. 139.11

Beil. Ref. VI, 226.



**Use:** Detection of ammonium, magnesium and potassium.

Determination of nitrate.

*p*-Nitrophenol consists of colorless to slightly yellow, odorless crystals, which have a sweetish and then a burning taste. The compound melts at 113-114° C. It sublimes on heating and is slightly volatile in steam. It is moderately soluble in cold water, and freely soluble in alcohol, chloroform and ether.

**Preparation:** *p*-Nitrosophenol: Dissolve 60 g. of phenol, 27 g. of sodium hydroxide and 54 g. of sodium nitrite in 1500 ml. of water. Cool the mixture to 7-8° C., and with further cooling add a mixture of 150 g. of concentrated sulfuric acid and 400 ml. of water. After 2 hours, filter the precipitated nitrosophenol, wash with water and dissolve in ether. Shake the ether solution with animal charcoal, filter, and remove the ether by evaporation. Quickly dry the yellow needles which are obtained, and purify by recrystallizing from benzene or toluene.<sup>1</sup>

*p*-Nitrophenol: Dilute 150 ml. of concentrated nitric acid with 450 ml. of water and heat 400 ml. of this solution to 40° C. Then add gradually 50 g. of *p*-nitrosophenol<sup>1</sup> in small portions. Allow to stand until the mass crystallizes. Separate the crystals by filtration, and purify by recrystallizing from water containing a little animal charcoal.<sup>2</sup>

**Detection of potassium, ammonium and magnesium.** Rosenthaler<sup>6</sup> has studied the use of *p*-nitrophenol as a microchemical reagent for various cations. He has reported that characteristic crystals are obtained with potassium, ammonium and magnesium salts. Manganese, zinc, barium, strontium and calcium

must be absent. Frediani and Gamble<sup>4</sup> have studied the use of this compound as a microchemical reagent for potassium and have found it to be unsatisfactory.

**Determination of nitrate.** Andrews<sup>5</sup> has used *p*-nitrophenol as a color standard in the determination of nitrate with phenoldisulfonic acid. A solution containing 0.993 g. of *p*-nitrophenol per liter (0.1 mg. of N per ml.) is used. A measured volume of this solution is made alkaline and diluted to match the color obtained in the usual manner.

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2. W. Robertson, *J. Chem. Soc.* **81**, 1477 (1902).
3. L. Rosenthaler, *Mikrochemie*, **2**, 29-32 (1924); *C.A.* **18**, 2481 (1924).
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## PICRIC ACID

Synonym: 2,4,6-Trinitrophenol

$C_6H_3O_7N_3$

Mol. Wt. 229.11

Beil. Ref. VI, 265.



**Use:** Detection of aluminum, ammonia, barium, cadmium, calcium, cobalt, copper, cyanide, gold, iron, magnesium, manganese, mercury, nickel, potassium, silver, sodium, thallium and zirconium.

Determination of bismuth, cyanide, hydrogen, iron, potassium, silica, titanium and zirconium.

Acidimetric and iodometric standard.

Picric acid consists of pale yellow, odorless, intensely bitter crystals. It melts at 122-123° C., and explodes at about 300° C. It also explodes if rapidly heated, or by percussion. One g. of the solid dissolves in 78 ml. of cold water, 15 ml. of boiling water, 12 ml. of alcohol, 10 ml. of benzene, 35 ml. of chloroform, and 65 ml. of ether.

For safety in transportation 10-20 per cent of water is usually added.

**Preparation:** Heat together 25 g. of phenol, and 68 ml. of concentrated sulfuric acid on a water-bath for one-half hour until a clear solution is obtained. Dilute with 100 ml. of water, well cooled, and pour into a 1-liter flask. Then add slowly from a separatory funnel, 50 ml. of concentrated nitric acid in small portions, and shake well. When all the nitric acid has been added, place the flask on a water bath and heat with the addition of 20 ml. of concentrated nitric acid for a period of 1 to 2 hours. Picric acid separates as a yellow crystalline mass on cooling. Dilute with water, filter with suction, and wash well with cold water. Purify by recrystallization from a large quantity of hot water that has been acidified with a few drops of sulfuric acid.<sup>1</sup>

**Detection of potassium.** Picric acid reacts with solutions of potassium salts to yield yellow crystalline needles which may be used for the microdetection of potassium.<sup>2-9</sup> Reichard<sup>4</sup> and Lutz<sup>6</sup> suggested the use of a 10 per cent

solution of sodium picrate as the reagent. According to Lutz,<sup>6</sup> 5.9 mg. of potassium per ml. is the smallest quantity that can be detected by a macromethod, although Caley<sup>5</sup> has reported that the reaction is sensitive to 0.8 mg. per ml. Orlenko and Fessenko<sup>8</sup> used a saturated aqueous solution of picric acid as the reagent, and studied the reactions of this compound with 21 cations. They report that precipitates characteristic under the microscope are obtained with ammonium, sodium, magnesium, barium, strontium, lead, zinc, nickel, mercurous, mercuric and silver ions. Chamot and Mason<sup>10</sup> state that rubidium, cesium, ammonium and thallous ions yield insoluble precipitates when treated with an alcoholic solution of picric acid to which sufficient water has been added to prevent the spreading of the drop when placed on the microscope slide.

Frediani<sup>2</sup> has studied the use of picric acid as a reagent for potassium, and has reported the following results: The reagent used was prepared by saturating 10 ml. of a 50 per cent alcoholic solution with picric acid, and then diluting with an equal volume of glycerol to retard evaporation and prevent spreading. Picric acid alone crystallizes from this solution as broad yellow plates and tablets. The potassium salt, however, forms rapidly as long, sharp, yellow needles. The sensitivity reported in this test is 0.2γ of potassium. Ammonium, rubidium and thallium ions give precipitates which are similar to those with potassium. Antimony yields colorless, feathery crystals, and bismuth also yields a crystalline precipitate. Very fine granulated precipitates are obtained with cesium and with both stannous and stannic tin. Negative tests were obtained with aluminum, arsenic, barium, cadmium, calcium, cobalt, chromium, copper, iron, lead, lithium, magnesium, manganese, mercurous, mercuric, nickel, silver, sodium, strontium and zinc ions.

Caley<sup>5</sup> considers the picric acid reaction a useful confirmatory test for potassium, and claims it is more sensitive than tests with perchloric acid, chloroplatinic acid and tartaric acid, but that it is not as delicate as the sodium cobaltinitrite test. The reagent recommended by Caley is prepared as follows: dry the moist compound in an oven at 70-80° C., recrystallize from benzene, allow to drain, and then let stand until the benzene evaporates. Then form from this reagent a saturated solution in 95 per cent alcohol. Caley also recommends that the volume of the reagent solution should be about 7-8 times that of the solution to be tested. Sodium is said to interfere with this test.

Minovici and Ionescu<sup>9</sup> have substituted a saturated solution of picric acid in ethyl malonate for the sodium picrate solution which has been recommended by Reichard<sup>4</sup> as a reagent for potassium.

**Determination of potassium.** Caley<sup>18</sup> has proposed a colorimetric method for the determination of potassium which is based upon the color of the solution of potassium picrate in water.

**Procedure.** Evaporate the solution containing potassium as the chloride to dryness on a steam bath. Dissolve the residue in 1 ml. of water, and add 7.5 ml. of a saturated solution of picric acid in 95 per cent ethyl alcohol. Stir until the precipitate begins to form, and allow the mixture to stand at 20° C. for 45 minutes, stirring regularly at 5 minute intervals. Filter through a medium sintered glass filtering crucible, and wash with 1-2 ml. portions of ether until

the washings are colorless. This usually requires from 5-10 washings. Dissolve the precipitate from the crucible with water and cool the resulting solution in a 50-ml. volumetric flask. Dilute to the mark, and compare the color of the solution with that obtained using solutions containing known quantities of potassium.

Best results are obtained in the above procedure by carrying out the precipitation at 12-15° C. Stirring for 10-15 minutes after the addition of the reagent yields larger crystals, which are best filtered through a plug of glass wool in an ordinary funnel.

Calcium, magnesium, aluminum, iron, phosphorus and silicon do not interfere, but if the quantity of sodium present is greater than twice that of potassium, the results obtained are inaccurate.

Bolliger<sup>15</sup> has determined the solubility of various picrates in different organic solvents, and his results are listed in Table 6.

TABLE 6.—SOLUBILITY OF PICRIC ACID AND PICRATES IN VARIOUS SOLVENTS AT 24° C.

Salt	Ethyl Alcohol %	Ethyl Ether %	Acetone %	Water %	Methyl Alcohol %
Potassium picrate .....	0.029	Below 0.00001	1.02	0.4	0.22
Ammonium picrate .....	0.62	0.004	....	...	1.67
Sodium picrate .....	2.2	0.001	....	10	12.
Calcium picrate .....	60.0	0.23	....	45	about 70.
Picric acid .....	6.2	2.0	....	1.2	0

From the above table it may be observed that the use of calcium picrate makes possible more favorable conditions for the precipitation and isolation of potassium picrate. Since calcium picrate is approximately 10 times as soluble in ethyl alcohol as picric acid, which has frequently been used as the reagent, the use of the calcium salt virtually eliminates any danger of contaminating the precipitate with the precipitating reagent.

Methylene blue reacts with picric acid to form a well-defined picrate which is only slightly soluble in water, but which dissolves readily in chloroform. The fact that methylene blue picrate can be extracted with chloroform, although methylene blue and picric acid are both insoluble in this solvent, makes possible the titration of picric acid, and indirectly potassium, by means of a standard solution of methylene blue.<sup>15-17</sup> Potassium is precipitated from a concentrated neutral solution by the addition of about 10 volumes of a 25 per cent calcium picrate solution in absolute alcohol. The precipitate is then dissolved in hot water, and is finally titrated with 0.001 N methylene blue solution. Solutions containing from 0.04 to 10 mg. of potassium, and not to exceed twice as much sodium, can be determined with an accuracy of approximately 1 per cent of the true value.

**Reagent.** *Calcium picrate:* Add 23 g. of picric acid and 10 g. of calcium carbonate to 100 ml. of water and boil until there is no longer any evolution of carbon dioxide. Filter and evaporate the filtrate to dryness. Dissolve in absolute alcohol and dilute to 100 ml. with this solvent. Filter before using.

*0.01 N methylene blue:* Dissolve 3.74 g. of methylene blue (C.P.  $C_{16}H_{18}N_3SCl \cdot 3H_2O$ ) in water and dilute to 1 liter.

**Procedure.** The material to be analyzed must not contain more than twice as much sodium as potassium, and the potassium must be present as the chloride or the perchlorate. Ammonium salts must be removed, although calcium and magnesium do not interfere.

Dissolve the sample in the smallest possible quantity of warm water, and if the material consists largely of potassium salt, add about 10 volumes of the calcium picrate solution. Mix well and allow to stand for 2 hours. If sodium and potassium are present in approximately equal quantities, add 20-30 volumes of calcium picrate solution, stir well, and allow to stand overnight in a stoppered bottle. In either case, filter through a fritted glass filter plate (medium) and wash as follows:

If the precipitate consists essentially of potassium picrate, wash repeatedly with about 4 volumes of ether containing 4 per cent ethyl alcohol until washings with pure ether remain colorless after remaining in contact with the precipitate for 10 minutes.

If appreciable quantities of sodium are present, the ether washings will remain yellow, and the precipitate of sodium picrate must be extracted with ethyl alcohol which has been saturated with potassium picrate.

After washing, dissolve the precipitate in hot water, transfer to a separatory funnel, containing 10 ml. of chloroform for each 100 ml. of potassium picrate solution, and titrate with standard methylene blue solution from a buret. Methylene blue picrate is only slightly soluble in water, but is extracted with chloroform which is added to the mixture in the separatory funnel. The end point of the titration is reached when the aqueous layer becomes colorless. On the addition of an excess of methylene blue, the aqueous layer becomes blue; hence, the practical end point is the faint appearance of a blue color in the aqueous layer.

The titration may be completed with 0.001 N methylene blue solution. The methylene blue solution is standardized against a known quantity of potassium treated in the same manner as described above.

**Detection of cyanides.** Cyanides may be detected by a procedure which depends upon the formation of a reddish-brown color which appears when a cyanide is added to an alkaline picrate solution. The reddish color is due to the formation of the sodium or potassium salt of isopurpuric acid, which is 4,6-dinitro-2-amino-3,5-dicyanophenol.<sup>18-20</sup> This color appears to have been observed originally by Hlasiwetz,<sup>21</sup> and has since been used by many investigators for the detection of small quantities of cyanides.<sup>22-29,39</sup>

The presence of certain reducing substances, which cause the development of a red color in alkaline picrate solutions, may cause interference with this

method. Sulfides, hydrosulfides, aldehydes, ketones and reducing sugars are included in this list. The test is carried out as follows:

**Procedure.** Place 3 ml. of a saturated picric acid solution in a test tube and add 1 ml. of 5 per cent sodium carbonate solution and 1 ml. of the solution to be tested. Heat in a boiling water-bath for 5 minutes, and allow to cool. A reddish-brown color appears if cyanides are present.

Wastenon<sup>30</sup> has used this reaction for the detection of cyanides in iodides:

**Procedure.** Add a drop of a 1:250 picric acid solution to 2 ml. of the solution of the iodide to be tested and warm. A red color may be observed with as little as 0.04 per cent hydrogen cyanide. The color is very pronounced if 0.1 per cent or more of hydrogen cyanide is present. Ammonium salts interfere.

Guignard<sup>23,24</sup> and Chelle<sup>31</sup> recommend for the detection of cyanides a test paper prepared by impregnating filter paper with a solution of 0.5 g. of picric acid and 5 g. of sodium carbonate per liter. By using picrate paper, 0.0052 mg. of hydrogen cyanide in 5 ml. of solution can be detected. The test is more sensitive at higher temperatures. Steyn<sup>32</sup> has found that if the test is carried out at about 60° C. for one and one-half hours, and then at 37-38° C. for an additional 16 hours, the test is more sensitive than when carried out at 30° C. for one and one-half hours and 15-20° C. for an additional 16 hours.

The picrate paper test gives very satisfactory results when applied to the detection of cyanides in plants, but the results are unreliable on human organs and other materials likely to contain reducing substances. In such cases the formation of ferric thiocyanate is the most reliable and the most sensitive.

Several investigators<sup>33-36</sup> have studied the various methods which have been proposed for the detection and determination of cyanides and the consensus of opinion appears to be that the picric acid method is neither specific nor sensitive. Approximately 0.4 mg. of cyanide in 10 ml. of solution can be detected with the use of picric acid at a dilution of 1:2450, and according to Anderson<sup>35</sup> this is the least sensitive of the various methods studied.

**Determination of cyanides.** In the presence of an excess of alkaline picrate, the development of the red color with cyanides is quantitative, thereby making possible the colorimetric determination of small quantities of cyanides. The following procedure is recommended by Smith:<sup>18</sup>

**Procedure.** Pipet 3 ml. of a saturated picric acid solution, 1 ml. of a 5 per cent sodium carbonate solution and 1 ml. of the cyanide solution to be tested into a tube having a 25-ml. graduation. Heat in a boiling water-bath for 5 minutes, cool in running water, and dilute to 25 ml. Compare the resulting color in a colorimeter with a standard solution prepared in an identical manner. The standard is prepared from 1 ml. of N/500 potassium or sodium cyanide, and the depth of the solution in the colorimeter is made 20 mm.

The accuracy of this method is said to be within 1 per cent of true value. Reducing substances such as sulfides, hyposulfides, aldehydes and ketones interfere.

Francois and Laffitte<sup>37</sup> have employed a picrate test paper for the determination of small quantities of cyanides. The paper is prepared according to the method of Guignard.<sup>27,31,32</sup>

**Reagent.** Impregnate filter paper with a solution prepared by dissolving 0.5 g. of picric acid and 5 g. of sodium carbonate in 1 liter of water.

**Procedure.** Place 1 ml. of a slightly acidified solution to be tested in a test tube and close the tube with a paraffined cork from which is suspended a moist strip of the sodium picrate paper prepared as described above. Allow to stand for 24 hours at room temperature, and compare the color of the paper with that of control strips exposed in the same manner to solutions containing known quantities of cyanide. As little as 0.002 g. of hydrogen cyanide per liter can be determined in this manner.

In the presence of starch or ammonia and ammonium compounds, the values obtained by this method are somewhat low. Ethyl alcohol, castor oil, liver and thymus tissue do not cause any interference. Heart tissue causes the fixation of a part of the hydrogen cyanide and thereby causes considerable error. In general the method has considerable application in plant physiology and in toxicology.

Chapman<sup>38</sup> has studied the reaction of cyanides with alkaline solutions of picric acid, and reports that the test depending upon this reaction is not reliable. The color may be due to the formation of an alkali salt of picramic acid by reducing substances, and also to the formation of the alkali salt of isopurpuric acid by hydrogen cyanide. The isopurpurate can be formed only when hydrogen cyanide is present in considerable quantity, and when the reacting solution is only faintly alkaline. Despite these claims, however, satisfactory results are reported by many investigators.<sup>22,39-48</sup> These procedures apply to the detection of cyanides in plant materials, since results generally are unreliable when applied to animal tissues.

**Determination of silicon.** Silicon may be determined colorimetrically by a method which is based upon the formation of highly colored, yellow silicomolybdic acid when a dilute solution of silica is treated with an acid and ammonium molybdate. The yellow color which develops in this reaction exactly matches that of dilute picric acid solutions; consequently solutions of picric acid may be employed as artificial standards in the colorimetric estimation of silica.<sup>49-56</sup>

Dienert and Wandenblucke<sup>49</sup> report that a solution containing 36.9 mg. of pure picric acid per liter gives a color equivalent to 50 mg. of  $\text{SiO}_2$ . Thresch and Beale<sup>50</sup> recommend a solution containing 40 mg. of picric acid per liter as giving a color identical to 50 mg. of  $\text{SiO}_2$ . King and Lucas<sup>55</sup> prepared their standard by dissolving 25.6 mg. of vacuum-dried picric acid in 1 liter of solution. This gives a color which corresponds to 50 mg. silica per liter. From the variation in methods of preparing the standards, some doubt arises as to the accuracy of their application.

The picric acid used in the preparation of these solutions should be crystallized from benzene by the method of Benedict<sup>56</sup> and then dried to constant weight in a vacuum desiccator.

Recently Galakhov<sup>54</sup> has prepared light filters for the colorimetric determination of silica by applying gelatine solutions of picric acid to glass.

**Determination of titanium and iron.** Galakhov<sup>54</sup> has mixed picric acid with Congo red for the preparation of filters for the determination of titanium and iron. These filters can be used instead of standard color solutions.

**Detection of ammonia.** Picric acid reacts with ammonia to form characteristic crystals which may be used for the identification of as little as 0.1γ of ammonia.<sup>8,11,57,75</sup> A saturated solution of picric acid in ethyl malonate or in alcohol containing 5 per cent of glycerol may be used as the reagent. Yellow characteristic crystals are obtained when this solution is exposed to ammonia fumes.<sup>58</sup>

Kollo and Teodossiu<sup>59</sup> have modified this test as follows:

**Procedure.** Mix a drop of formaldehyde and 1 drop of 1 per cent picric acid solution, and expose to the gas suspected of containing ammonia. Some urotropine is formed in this reaction and this combines with picric acid to form prismatic yellow crystals which can be identified under the microscope.

A precipitate of somewhat uncertain composition containing ammonia, copper and picric acid, and which has a characteristic appearance under the microscope, is formed when a mixture of picric acid and copper sulfate is exposed to ammonia gas. This reaction may be used as a test for copper, ammonia and picric acid:<sup>60</sup>

**Procedure.** Mix a saturated aqueous solution of picric acid with an equal volume of 0.1 per cent copper sulfate solution and expose a drop of this mixture to the gas suspected of containing ammonia. Characteristic crystals are formed with as little as 2 mg. of ammonia.

This reaction can be used for the detection of ammonia in pyridine.

**Detection and determination of zirconium.** When powdered picric acid is added to a solution of zirconium oxychloride, a precipitate is formed which may be examined under the microscope for the detection of zirconium. This precipitate appears at first to consist of a basic picrate  $\text{ZrO}(\text{C}_6\text{H}_2\text{O}_7\text{N}_3)_2$ , but this later upon hydrolysis is converted to zirconium hydroxide and the picric acid passes into solution. The solution from which the precipitation is carried out should be faintly acid with hydrochloric acid. The test is not satisfactory in the presence of sulfates or nitrates; in such cases zirconium is precipitated with ammonium hydroxide, and the resulting hydroxide dissolved in hydrochloric acid before testing with picric acid.<sup>61</sup>

Precipitation of zirconium as the picrate is quantitative, and this reaction may be used for the determination of zirconium.<sup>62</sup> The precipitate of zirconium picrate is moistened with sulfuric acid before ignition to prevent loss by the explosion of the compound. The solubility of the zirconium precipitate in mineral acids makes impossible the complete separation of zirconium from iron and aluminum. Further, since thorium dioxide can not be separated from zirconium dioxide, the picrate method for determining zirconium seems to be of little value.



**Detection of copper.** Characteristic hexagonal crystals of cupric ammonia picrate may be used for the identification of small quantities of copper. The following test is proposed by Shead:<sup>63</sup>

**Procedure.** Make the solution containing copper slightly alkaline with ammonium hydroxide, and add dropwise a boiling ammoniacal solution of ammonium picrate until a crystalline precipitate appears. Most satisfactory results are obtained when the solution is approximately 0.005 M in copper and ammonium picrate, and about 0.1 M in ammonia. A small test tube should be used for the procedure, and the final volume of the mixture should not exceed 5 ml. A positive test is obtained with solutions that are 0.001 M in copper salt, although 5-10 minutes are required for the formation of the crystals.

A reagent consisting of 2 parts of saturated aqueous picric acid and 1 part of 10 per cent ammonia may be used for the detection of 0.05% of copper. A bright greenish-yellow precipitate is obtained when the above reagent is added to a solution of a copper salt.

**Determination of bismuth.** Bismuth can be separated from lead by making the solution slightly acid with nitric acid, adding an excess of picric acid, and neutralizing to methyl orange with ammonium carbonate. Bismuth is precipitated as  $\text{Bi}(\text{OH})_2 \cdot \text{OC}_6\text{H}_2(\text{NO}_2)_3$ . The compound is explosive and cannot be heated and weighed, but it is readily converted to  $\text{Bi}_2\text{O}_3$ , which is suitable for weighing. If the bismuth oxide content is greater than 0.01 g., the precipitate is converted to bismuth carbonate by boiling with ammonium carbonate, or is dissolved in nitric acid, evaporated, and ignited and weighed as  $\text{Bi}_2\text{O}_3$ . The separation of lead is unaffected by copper and cadmium, but is influenced by iron, phosphoric and arsenic acid.<sup>64</sup>

**Procedure.** To the bismuth solution containing about 3 ml. of 6 N nitric acid, add sufficient water to make the total volume 100 ml., and then add 100 ml. of a cold saturated aqueous solution of picric acid. Add a few drops of methyl orange indicator, and add ammonium carbonate solution until the indicator turns yellow. Filter, wash the precipitate with cold water, and dissolve in hot dilute nitric acid. Precipitate with ammonium carbonate, and ignite and weigh as  $\text{Bi}_2\text{O}_3$ . A double precipitation is recommended if a large quantity of lead is present.

**Detection of thallium.** Thallium may be detected microscopically by means of characteristic crystals which are formed when a solution of a thallos salt is treated with a saturated solution of picric acid.<sup>2,10,70,76,77</sup>

**Detection of sodium.** Sodium can also be detected by a microchemical method which depends upon the formation of crystals of sodium picrate.<sup>3,66</sup>

**Procedure.** Place a small drop of cold saturated solution of picric acid on a glass slide and add several particles of the salt to be tested, and without covering the slide examine under a microscope with a magnification of 100 diameters. The crystals of sodium picrate are easily distinguished.

**Microdetection of metals.** In preceding sections a number of microchemical methods have been described for the detection of various ions with picric acid. Ammonium, aluminum, silver, barium, calcium, ferric, magnesium and manganese ions yield crystalline compounds which, according to Frangopol,<sup>11</sup> can be used for the microchemical detection of these substances. Korenman<sup>12</sup> recommends a reagent prepared by mixing 2 parts of a saturated aqueous solution of picric acid with 1 part of 10 per cent ammonium hydroxide. In highly dilute solutions, this reagent produces precipitates with copper, silver, cobalt, nickel, cadmium, mercury and gold.

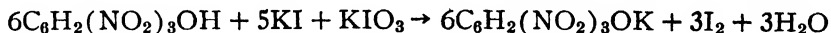
Results obtained in reactions of various cations with picric acid are given in Table 7.

TABLE 7.—DETECTION OF METALS WITH PICRIC ACID

Metal	Reaction	Sensitivity $\gamma$	Dilution Limit	Reference
Mercury .....	Yellow	0.15	1:100,000	12
Aluminum .....	Cryst.			11
Manganese .....	Cryst.			11
Nickel .....	Cryst.	0.1	1:100,000	12, 79
Cobalt .....	Cryst.	0.3	1:30,000	12, 79
Strontium .....	Yellow	60	1:160	3
Silver .....	Yellow-brown	20	1:500	3, 11, 12, 79, 80, 81
Magnesium .....	White	23	1:430	3, 11, 81
Copper .....	Green-yellow	0.01	1:1,000,000	79
Cadmium .....	Yellow	0.2	1:50,000	79
Lead .....	Orange-yellow			11, 79
Zirconium .....	Yellow	2	1:5,000	61, 62, 82
Gold .....	Cryst.	0.2		12, 78, 79
Thallium .....	Yellow			77
Ammonium .....	Yellow	3	1:33,000	3, 11, 81
Potassium .....	Yellow	4000	1:1,250	3, 4, 5, 6, 8, 10, 83, 84, 85
Sodium .....	Yellow	11	1:900	3, 66, 84
Barium .....	Yellow-white	23	1:430	3, 11, 81
Calcium .....	Yellow			11, 81

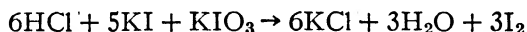
**Titrimetric standard.** Sanders<sup>67,68</sup> has proposed the use of picric acid as a standard in iodometry and acidimetry. The reagent can be obtained in very pure form, and is easily purified by recrystallizing from ethyl alcohol. It is not hygroscopic, and its purity is established by its melting point. Due to its insolubility, however, only 0.04 to 0.01 N solutions can be prepared.

Picric acid reacts with potassium iodide and potassium iodate as follows:



A solution of sodium thiosulfate can be standardized by titrating the iodine liberated in this reaction.

Picric acid solutions can not be titrated accurately against an alkali since the color of the organic compound obscures the end point with methyl orange. If, however, a known volume of hydrochloric acid is added to an excess of potassium iodide and potassium iodate and the liberated iodine titrated with standard thiosulfate, the strength of the acid can be calculated from the following equation:



Since sodium thiosulfate may be standardized against picric acid, the latter may serve as an indirect acidimetric standard. The iodometric standardization has the advantage of a sharper end point, although the procedure is somewhat more difficult than others which have been proposed.

**Determination of hydrogen.** Colloidal palladium is used in gas analysis for the adsorption of hydrogen. Colloidal palladium itself adsorbs large volumes of hydrogen, but if used in considerable quantity is quite costly. In the presence of an easily reducible substance such as sodium picrate, however, palladium acts only as a catalyst and may be used in smaller amounts than would be necessary if employed alone. Various solutions containing sodium picrate and colloidal palladium have been used as an absorbing agent for hydrogen in gas analysis.<sup>60-73</sup> Methods employing this reagent are said to be superior to combustion methods. Paal's<sup>69</sup> solution is prepared by dissolving 2 g. of sodium picrate and 2 g. of colloidal palladium in 100 ml. of water. Brunck<sup>71</sup> prepared a solution by neutralizing 22 ml. of N sodium carbonate with 5 g. of picric acid, and diluting to 100 ml. with water, and then adding 2 g. of colloidal palladium. Approximately 11.3 ml. of hydrogen is absorbed by 1 ml. of this solution.

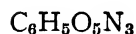
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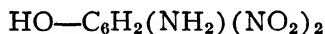
## PICRAMIC ACID

Synonym: 4,6-Dinitro-2-aminophenol



Mol. Wt. 199.12

Beil. Ref. XIII, 394.



**Use:** Detection of osmium. Color comparison.

This compound is a red, crystalline solid which melts at 169° C. It is soluble in 715 parts of water, and is readily soluble in alcohol, benzene, glacial acetic acid and aniline. It is only slightly soluble in chloroform and ether.

**Preparation:** Dissolve 10 g. of picric acid and 10 g. of sodium hydroxide in 600 ml. of water, and heat to 55° C. With vigorous stirring, add gradually a solution of 40 g. of sodium sulfide ( $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ ) in 100 ml. of water. Then add gradually 127 g. of powdered picric acid alternately with 220 g. of sodium sulfide dissolved in 400 ml. of water. The sodium sulfide and picric acid should be added at such rate that the last of each is added at the same time. The temperature should not rise above 65° C., and if the mixture becomes warmer, add ice. Continue to stir for 10 minutes after the addition of the reagents, and quickly add 400 g. of ice. The sodium salt of picramic acid is precipitated. Allow to stand 10 hours, filter, and wash with brine.

To obtain the free acid, stir the sodium salt with 500 ml. of water, heat to 80° C. and add dilute sulfuric acid until the mixture is acid to Congo red.<sup>1</sup>

**Analytical uses.** The use of picramic acid in colorimetric work offers many advantages over the colorations produced by picric acid combinations.

A black coloration is obtained when osmic acid is treated with picramic acid.<sup>2</sup>

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**PICROLONIC ACID**

Synonym: 1-(4-Nitrophenyl)-3-methyl-4-nitropyrazolone-5

 $C_{10}H_8O_5N_4$ 

Mol. Wt. 264.20

Beil. Ref. XXIV, 51 (218).

**Use:** Detection of ammonium, calcium, copper, mercury potassium, sodium, and strontium.

Determination of calcium, lead, magnesium and thorium.

Picrolonic acid is a yellow crystalline solid which melts at 116-117° C. It decomposes at 125° C. It is sparingly soluble in water, but dissolves readily in alcohol.

**Preparation:** Place 600 ml. of 90 per cent nitric acid ( $d = 1.49$ ) in a wide-mouth bottle and cool with ice water. Then add 200 g. of methylphenylpyrazolone, 1 g. at a time with mechanical stirring, and with the temperature maintained below 15° C. When all the methylphenylpyrazolone has been added, continue to stir for 30 minutes, and then filter through a porcelain disc covered with asbestos. Apply suction to remove most of the acid, and wash, first with dilute nitric acid, and finally with water.

Place 1500 ml. of 33 per cent acetic acid in a beaker on a water-bath, and stir mechanically while adding the finely ground product obtained in the above reaction. The temperature should not exceed 60° C. A mass of light yellow flocculent crystals forms at a temperature between 50° and 60° C. After about 40 minutes, filter through a Büchner funnel, wash with water, and grind the product in a mortar with 150 g. of crystalline sodium carbonate. Press out the sodium salt and crystallize from a mixture of 3 volumes of ethyl alcohol and 1 volume of water. Decompose the sodium salt with concentrated hydrochloric acid. Warm the acid in a beaker on a water-bath, and stir while adding the sodium salt in small portions. Filter the crystalline product through a porcelain disc covered with asbestos, using suction, and wash with water to remove sodium chloride. Purify by recrystallizing from ethyl alcohol.<sup>1</sup>

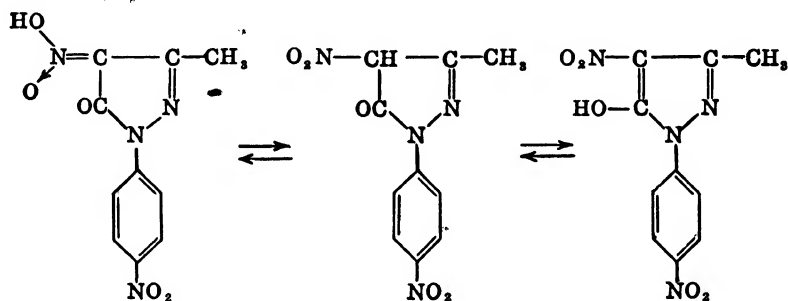
Pure picrolonic acid is prepared by recrystallizing the commercial product from 33 per cent acetic acid, and then from alcohol.

**Solubility of picrolonic acid.** Solubility measurements by various investigators indicate that, depending on the method used in preparing the solution, apparently saturated solutions of picrolonic acid have different concentrations. Hugounenq and co-workers<sup>27</sup> report the solubility of the acid as 1.2 g. per liter at 17° C. Kisser,<sup>2</sup> however, refers to a 0.01 N solution, which corresponds to a concentration of 2.64 g. per liter, and others mention solutions of even higher concentration. According to the studies of Dworzak and Reich-Rohrwig,<sup>5</sup> a saturated solution of picrolonic acid is 0.01 N. When the solution is prepared by allowing the acid to stand for several weeks in contact with cold water, the concentration is always distinctly less than 0.01 N. If, however, the solution is prepared by adding water to the acid while warming with frequent stirring on a water bath, then cooling overnight and filtering, and finally diluting to 1

liter with water, the concentration is very nearly 0.01 N. More concentrated solutions can be prepared, but these are obviously supersaturated, since picrolonic acid separates on standing.

**Reactions of picrolonic acid.** Picrolonic acid forms a number of slightly soluble metal salts. The calcium, lead and thorium salts are especially suitable for gravimetric determinations. Methods based on the formation of these compounds are particularly useful in microanalysis, because the precipitates are readily freed of impurities by washing, and also because they are rapidly dried in a stream of air. Further, the precipitates have high molecular weights, and consequently favorable conversion factors, and this makes possible the determination of small quantities of the metals with great exactness.

Three possible tautomeric structures have been assigned to picrolonic acid.



Both structures I and III will account for the acidic properties of the picrolonic acid molecule, although structure I containing the *aci*-form of the nitro group seems the more probable. A salt could possibly be formed from structure II, but in this case it must be assumed that the *p*-nitrophenyl group forms a coordinate bond with the metal atom. The resulting salt would then necessarily have the properties of an inner-complex, but the color and solubility of calcium picrolonate, for example, seemingly eliminates this possibility.

Picrolonic acid is of particular interest in analytical chemistry, since it forms colored precipitates with the alkaline earths, notably calcium, for which there is a decided lack of useful organic reagents.

In general picrolonic acid resembles oxalic acid in its analytical properties. It is not very selective in its action, and the alkali salts are much less soluble than the corresponding oxalates. This is a disadvantage, but the picrolonates are more characteristic under a microscope, which makes the reagent somewhat more useful for the detection of the alkaline earths than oxalic acid.

**Detection of the alkaline earth metals.** Picrolonic acid forms characteristic crystals with calcium salts which are easily recognizable under a microscope. A solution containing 0.264 g. of picrolonic acid in 100 ml. of water can be used as a sensitive reagent for calcium. Both lead and copper form insoluble precipitates, but they have no influence upon the crystals of the calcium compound.<sup>2</sup>

Strontium as well as calcium yields crystals with picrolonic acid, but the calcium and strontium compounds may be differentiated by a procedure proposed by Fischer.<sup>3</sup>

The crystals obtained by the cautious evaporation of a mixture of a drop of the test solution and reagent on a microscope slide are washed with chloroform and water, and the melting point determined. The calcium salt melts at 250-270° C., but not sharply. The strontium salt does not melt at temperatures below 350° C. By making use of this difference in the melting points of the calcium and strontium compounds, as little as 0.2% of strontium or calcium can be detected by reaction with picrolonic acid.

**Reagent.** Dissolve picrolonic acid in dried chloroform and evaporate in vacuum over sulfuric acid. Dissolve the residue in pure water.

**Procedure.** Mix a small drop of the solution to be tested with a small drop of the reagent and evaporate slowly with moderate warming. Remove the excess reagent by washing with alcohol-free chloroform and then with cold water. The calcium or strontium can be detected by means of characteristic crystals which form.

The strontium test may be carried out in the presence of relatively large quantities of barium and calcium.<sup>25</sup>

The solubility and composition of the alkaline earth picrolonates are given in Table 8.<sup>4</sup>

TABLE 8.—SOLUBILITY OF THE ALKALINE EARTH PICROLONATES

Salt	Formula	Solubility mg. per 100 ml. at 18°
Calcium .....	$\text{Ca}(\text{C}_{10}\text{H}_7\text{N}_4\text{O}_5)_2 \cdot 8\text{H}_2\text{O}$	0.5
Magnesium .....	$\text{Mg}(\text{C}_{10}\text{H}_7\text{N}_4\text{O}_5)_2 \cdot 2\text{H}_2\text{O}$	0.3
Strontium .....	$\text{Sr}(\text{C}_{10}\text{H}_7\text{N}_4\text{O}_5)_2 \cdot 7\text{H}_2\text{O}$	1.4
Barium .....	$\text{Ba}(\text{C}_{10}\text{H}_7\text{N}_4\text{O}_5)_2 \cdot 4\text{H}_2\text{O}$	2.5

**Determination of calcium.** A precipitate of  $\text{Ca}(\text{C}_{10}\text{H}_7\text{N}_4\text{O}_5)_2 \cdot 8\text{H}_2\text{O}$  is formed when picrolonic acid is added to a neutral solution of a calcium salt. This precipitate can be dried in air and weighed in this form. It contains 5.64 per cent of calcium, and can be formed in the presence of moderate amounts of magnesium and the alkali salts.

The following method is used for the gravimetric determination of calcium.

**Procedure.** Make the solution containing not more than 0.1 g. of calcium neutral to litmus, and warm to 50° C. Add dropwise from a buret a 0.01 N aqueous solution of picrolonic acid until a precipitate forms. If this is flocculent, warm and shake the mixture until the precipitate becomes coarse and crystalline. Continue the addition of the reagent at such rate that further precipitation yields a crystalline product. Should the precipitate be flocculent, however, again interrupt the addition of the reagent and convert to a crystalline form as before.



Continue to add picrolonic acid until no more precipitate forms, and then add a quantity of picrolonic acid equal to one-half the volume of the reaction mixture. Allow to stand several hours in a cool place, and transfer the precipitate to a filter crucible. Wash twice with cold water, and dry the precipitate to constant weight by sucking through it a stream of dust-free air. This usually requires 1-2 hours. The factor for calcium is 0.05641.

This method can also be applied to the microdetermination of 25 $\gamma$  of calcium in 2 ml. of solution.<sup>5</sup>

Tanii<sup>6</sup> has studied the precipitation of calcium with picrolonic acid and claims that the proper pH range for the precipitation is 2-3.

Bolliger<sup>7,8</sup> has determined calcium by precipitating with a measured excess of picrolonic acid, and then titrating the excess with methylene blue. More recently Cohn and Kolthoff<sup>9</sup> have studied the determination of calcium using picrolonic acid by means of an amperometric titration and a methylene blue titration. Bolliger titrated picrolonic acid with methylene blue and removed the insoluble methylene blue picrolonate from the aqueous solution by means of chloroform in which it is readily soluble. The titration is carried out in the presence of a phosphate buffer or sodium carbonate. The end point is reached when chloroform fails to remove the blue-green color formed in the aqueous layer upon the addition of a few drops of methylene blue. Since methylene blue picrolonate is markedly soluble in water, the chloroform must be replaced frequently in the titration, and near the end point it must be removed several times after each small addition of the titration liquid until it remains practically colorless upon being shaken with the aqueous phase. An amperometric determination gives results which are comparable to those obtained with the methylene blue titration.

Schiedwitz<sup>10</sup> determined the excess picrolonic acid by converting to the acridine salt. Acridine picrolonate has the advantage of low solubility and high molecular weight.

According to Cohn and Kolthoff,<sup>11</sup> calcium can be determined over a concentration range of 0.001-0.01 M by precipitating as calcium picrolonate with a slight excess of standard picrolonic acid under specified conditions, and then estimating the excess polarographically without filtering. An accuracy of 1-2 per cent is claimed, and good results are obtained in the presence of relatively large amounts of sodium, potassium, ammonium, magnesium, sulfate and phosphate.

Alten and co-workers<sup>12</sup> have suggested a method for the colorimetric determination of about 0.15 mg. of calcium per ml. by precipitating as calcium picrolonate, and treating the precipitate with bromine water and sodium hydroxide. A dilute solution of picrolonic acid gives a turbidity with bromine water, but this cannot be used for the nephelometric determination of the former. After removing the excess bromine and treating with sodium hydroxide, however, the turbidity disappears with the formation of a red color.

The color is proportional to the concentration of picrolonic acid. The red color varies somewhat between red and yellowish red, and is stable in the dark for at least 48 hours.

Magnesium, potassium, sodium and ammonium ions do not interfere. Iron and aluminum must be removed or kept in solution by means of sulfosalicylic acid.

**Reagent.** Dissolve 2.64 g. of picrolonic acid in 1 liter of water. Warm on a water-bath, allow to stand over night and filter.

**Procedure.** The solution to be analyzed must be only slightly acid. Any excess of acid should be removed by evaporation. Place 5 ml. of the solution to be analyzed in a 10-ml. volumetric flask and neutralize with sodium hydroxide, using methyl orange as the indicator. Add 1 drop of 10 per cent sulfosalicylic acid and dilute to 10 ml. Filter and place 1-2 ml. of the filtered solution in a centrifuge tube having an interior diameter of 12 mm., and mix with 3 times as much ice-cold reagent solution. Allow to stand and filter through a porcelain filter stick (B II). Remove the adhering picrolonic acid solution by washing three times with anhydrous ether, and then pour hot water over the precipitate until the filter stick is covered. Then transfer the calcium picrolonate solution to a 50-ml. flask.

To the picrolonate solution, corresponding to 20-150 $\gamma$  of calcium, in a 50-ml. volumetric flask, add 1 ml. of saturated bromine water, and heat 10 minutes on a water-bath. Next add 10 ml. of alcohol, allow to cool for one-half hour, and mix with 2 ml. of 2 N sodium hydroxide solution. Compare the resulting colors with standards similarly prepared.

Van Slyke and Kreysa<sup>13</sup> have determined calcium indirectly in organic matter by precipitating as the picrolonate, and then estimating the carbon in the precipitate by rapid manometric, wet combustion method. The precipitate of calcium picrolonate contains 20 carbon atoms for each atom of calcium. Smaller quantities of calcium can be determined more accurately by this method than by the usual procedures based upon the titration of the precipitated oxalate. The determination can be used with 0.2 mg. of calcium or 0.2 ml. of serum.

**Determination of magnesium.** Bolliger<sup>14</sup> has applied the methylene blue titration to the determination of small quantities of magnesium. A known quantity of standard lithium picrolonate is added to an aqueous solution containing magnesium ions, and, after heating and evaporating, the excess reagent is titrated with 0.01 N methylene blue. In general the procedure resembles that used for the determination of calcium.

**Determination of lead.** Picrolonic acid reacts with solutions of lead salts to form a precipitate corresponding to the formula  $\text{Pb}(\text{C}_{10}\text{H}_7\text{N}_4\text{O}_8)_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ . The solubility of this compound corresponds to 7 mg. of lead per liter of water at 0° C. The reaction is most satisfactorily carried out in a solution that is neutral to litmus, and which has a volume of about 50 ml. for each 0.1 g. of lead. Only small quantities of alkali and ammonium salts should be present. The precipitant is prepared by dissolving 2.64 g. of picrolonic acid in a liter of solution. The method is particularly suitable for determining lead in the presence of small quantities of platinum, such as are present in solutions which

are obtained with the use of platinum vessels.<sup>15</sup> Tanii and co-workers<sup>6</sup> recommend a pH of 2-6.5 as the proper acidity for precipitating lead picrolonate.

Mahr and Ohle<sup>16</sup> have recommended the determination of lead as the picrolonate after previously precipitating with thiourea.

**Procedure.** Heat the solution to boiling in a large beaker, and then add for each 0.1 g. of lead 100 ml. of 0.01 N picrolonic acid solution. The reagent should be added dropwise and with constant stirring. Then add in a stream a volume of the reagent solution equal to one-half the volume of the reaction mixture. Place in a refrigerator until completely cold. Carefully transfer the precipitate to a filter crucible, using slight suction. Use the least possible quantity of ice-cold water for this purpose. Wash the precipitate with ice-cold water until the filtrate comes through colorless. About 50 ml. of water is usually sufficient. Dry at 130-140° C. to constant weight. The factor for lead is 0.27249.

This method may also be used for the microdetermination of small quantities of lead.

**Determination of thorium.** Picrolonic acid reacts with a solution of a thorium salt to form a precipitate of  $\text{Th}(\text{C}_{10}\text{H}_7\text{O}_5\text{N}_4)_4 \cdot \text{H}_2\text{O}$ . This salt is less soluble than the corresponding lead and calcium compounds, and is especially suited to microdeterminations.

It is impossible to separate thorium from the other rare earths with the aid of picrolonic acid, but after precipitating thorium as the hydrated peroxide by treating with ammonium nitrate and hydrogen peroxide, the precipitate can be dissolved in nitric acid and then precipitated with picrolonic acid.<sup>24</sup>

The following optimum conditions are recommended for the thorium determination:<sup>17</sup> free the solution containing thorium from ammonium salts and add 50 ml. of 0.01 N picrolonic acid for each 10 mg. of thorium in a volume of 55-60 ml., and containing 2.5 per cent acetic acid by volume.

Tanii<sup>6</sup> recommends a pH of 2.0-3.2 as the most suitable acidity for precipitating thorium picrolonate.

**Procedure.** Evaporate the sample solution to dryness to remove any free nitric acid, and then dissolve the residue in the smallest possible amount of water. This corresponds to about 5 ml. of water for each 10 mg. of thorium. Then add a quantity of acetic acid such that at the completion of the precipitation the acid concentration is 2.5-3 per cent by volume. Heat to boiling and add dropwise from a dropping funnel a 0.01 N solution of picrolonic acid with continuous boiling until a precipitate no longer forms. Then add all at once a quantity of the precipitant required to make the total amount used about 2.5 times that theoretically required; that is, about 50 ml. of 0.01 N picrolonic acid for each 10 mg. of thorium. Allow the mixture to stand about one hour in a refrigerator and filter through a filter crucible. Wash 3-4 times with several ml. of ice-cold water to remove the excess picrolonic acid. Dry to constant weight in a stream of dust-free air. The factor for thorium is 0.1782.

The microdetermination of thorium by a modification of the above method is one of the best so far proposed. It is reported to be more accurate than methods based on the determination of thorium as the oxide.

**Detection of alkali metals and ammonium salts.** An aqueous solution of picrolonic acid forms yellow precipitates with salts of the alkaline earth metals and with sodium, potassium and ammonium salts. No similar precipitate is obtained, however, with lithium. This permits the separation of lithium from the other alkali metals. The potassium salt is less soluble than the sodium salt, and the picrolonates are more insoluble than the corresponding picrates. Sodium picrate, for example, is water soluble.<sup>18,23</sup>

To detect sodium in a mixture of sodium and potassium salts, first precipitate potassium with a saturated solution of picric acid, and then add to the filtrate a few drops of 0.02 N picrolonic acid.

Long needles of picrolonic acid may separate from a saturated aqueous solution of the reagent, which is commonly used for the precipitation of potassium, but in the presence of potassium a yellow mass having no definite crystalline characteristics is formed, and this later changes to poorly formed needles. By means of this reaction 1γ of potassium can be detected.<sup>19</sup>

The test may be carried out as follows: <sup>26</sup>

**Procedure.** Add 1 drop of a 0.5 per cent solution of picrolonic acid in 50 per cent alcohol to a drop of test solution on a microscope slide. Warm gently and examine under a microscope. Yellow rods or needles form with sodium or potassium.

According to Martini,<sup>20,21</sup> 1γ of the ammonium ion can be detected by means of the microcrystals of ammonium picrolonate which form when ammonium salts are treated with picrolonic acid. These crystals show a characteristic behavior under a polarizing microscope. Ammonium ions can be detected in the presence of relatively large quantities of sodium and potassium.<sup>25</sup>

Only aluminum, chromium and lithium ions fail to give a positive test with picrolonic acid. Mercurous and mercuric ions yield yellow amorphous precipitates; copper, zinc, cadmium, arsenic and manganese form yellow rosettes of small needles; nickel and cobalt form small clusters of crystals; bismuth first forms a white amorphous precipitate, which later changes to a crystalline solid; trivalent arsenic, antimony and both stannous and stannic tin yield crystals of irregular shape; silver and cesium give small yellow rods; strontium and thallous salts give yellow crystalline precipitates; and ferric salts yield a microcrystalline precipitate. Ammonium salts yield a better test than potassium. Sodium, rubidium and lead are precipitated in the same manner as potassium.

**Detection of mercury and copper.** Picrolonic acid may also be used as a microchemical reagent for the detection of copper and mercurous ions. According to Martini,<sup>22</sup> satisfactory results are not obtained with copper, although the test is said to be very sensitive.

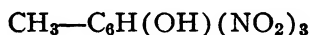
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## 2,4,6-TRINITRO-*m*-CRESOL



Mol. Wt. 243.13

Beil. Ref. VI, 387



**Use:** Detection of ammonium and potassium.

2,4,6-Trinitro-*m*-cresol is a yellow crystalline solid which melts at 106.5° C. It explodes when heated to 150° C. It dissolves readily in alcohol, ether, acetone and benzene, but is only slightly soluble in water.

**Preparation:** Dissolve *m*-cresol in 3 parts of concentrated sulfuric acid and allow the warm solution to stand until a sample on dilution with water dissolves without the separation of cresol. Then mix with water and a little nitric acid and heat. After the first vigorous reaction has subsided add more nitric acid

and evaporate until decomposition begins. Boil the residue with a little water, and finally recrystallize several times from alcohol.<sup>1</sup>

**Detection of potassium and ammonium.** Rosenthaler<sup>2</sup> has suggested the use of 2,4,6-trinitro-*m*-cresol as a microchemical reagent for the detection of potassium and ammonium. With potassium 2,4,6-trinitro-*m*-cresol forms long yellow rods with some branching at the end in a flowerlike spray. As little as 0.4γ of potassium can be detected in this way. No reaction is obtained with aluminum, arsenic, barium, cadmium, calcium, cobalt, chromium, copper, iron, lead, lithium, magnesium, manganese, mercuric mercury, mercurous mercury, nickel, strontium and zinc. Greenish-yellow crystals are obtained with sodium nitrate, and similar crystals are obtained with ammonium, cesium, rubidium, silver and thallous ions. Antimony trichloride yields colorless irregularly shaped crystals, as do tin and bismuth salts.<sup>3</sup>

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## 2,4,6-TRINITRORESORCINOL

Synonym: Styphnic acid

$C_6H_3O_8N_3$

Mol. Wt. 245.11

Beil. Ref. VI, 830

$(HO)_2C_6H(NO_2)_3$

**Use:** Detection of ammonium, potassium, and thallium.

2,4,6-Trinitroresorcinol is a yellow crystalline solid which possesses an astringent taste. It melts at 175.5° C. It is slightly soluble in water and is easily soluble in alcohol and ether.

**Preparation:** Add 1 part of finely powdered resorcinol in small portions to 5-6 parts of concentrated sulfuric acid heated to 40° C. Each portion should be dissolved completely before the next is added. Warm the mixture on a water-bath until 4,6-resorcinoldisulfonic acid separates as a paste. Cool and add nitric acid gradually at a temperature not exceeding 10-12° C. At first add concentrated nitric acid which has been diluted with 10 per cent of water, then add undiluted nitric acid and finally add fuming nitric acid. The total quantity of nitric acid should be 2-2.5 times the calculated quantity. Allow the mixture to stand overnight, and pour the yellow crystalline mass into 1.5-2 volumes of water. Decant the liquid from the light yellow crystalline mass which separates, and filter with suction. Wash until all sulfuric acid is removed, and finally dry on a water-bath.<sup>1</sup>

**Detection of potassium.** 2,4,6-Trinitroresorcinol may be used for the microchemical detection of potassium, ammonium, and thallium.<sup>2-4</sup> As little as 0.03γ of potassium is precipitated with this reagent. Aluminum, cadmium, calcium, cobalt, chromium, copper, lead, lithium, magnesium, nickel and zinc give negative tests. Ammonium, cesium, rubidium and thallous ions yield yellow plates and tablets. The cesium salt is the most soluble of this group. The thal-

lous salt is somewhat characteristic, since the crystals are irregularly shaped. Light yellow needles are formed in the presence of silver, sodium and strontium, while with arsenic, mercurous mercury, mercuric mercury and bismuth dendritic-shaped crystals are obtained. Antimony and barium form well-defined colorless crystals.

Manganese yields clusters of colorless rods. Fischer <sup>4</sup> claims that a precipitate is obtained with 0.1γ of ammonia.

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## CHAPTER II

### THE ARSONIC ACIDS

Like arsenic acid, the organic derivatives of arsenic acid react with zirconium salts in hydrochloric or nitric acid solutions to yield white amorphous precipitates of the zirconium arsonates. The reaction of zirconium with benzenearsonic acid,  $\text{C}_6\text{H}_5\text{—AsO(OH)}_2$ , was first announced by Rice, Fogg, and James.<sup>1</sup> Kapulitzas<sup>2</sup> investigated the precipitation characteristics of a number of the substitution products of benzenearsonic acid, and demonstrated that the ability of these compounds to precipitate zirconium is retained by many organic compounds containing the  $\text{—AsO(OH)}_2$  group. The tests conducted by Kapulitzas were carried out by using a saturated solution of the arsonic acid and 2 ml. of an acid zirconium solution. The arsonic acids used, and the limits of identification attainable are shown in Table 9.

TABLE 9.—REACTIONS OF DERIVATIVES OF BENZENEARSONIC ACIDS WITH ZIRCONIUM

Arsonic Acid	Formula	Molecular Wt.	Limit of Identification mg.
Acetarsanilic acid	$\text{CH}_3\text{COHN—C}_6\text{H}_4\text{—AsO(OH)}_2$	257.02	0.016
Arsanilic acid	$\text{H}_2\text{N—C}_6\text{H}_4\text{—AsO(OH)}_2$	217.03	0.06
<i>m</i> -Benzearsonic acid	$\text{HO}_2\text{C—C}_6\text{H}_4\text{—AsO(OH)}_2$	246.01	0.016
Biphenylarsonic acid	$\text{C}_6\text{H}_5\text{—C}_6\text{H}_4\text{—AsO(OH)}_2$	278.04	0.032
3-Chloroarsanilic acid	$\text{Cl(NH}_2\text{)C}_6\text{H}_3\text{—AsO(OH)}_2$	251.47	0.024
3,5-Dichloroarsanilic acid	$\text{Cl}_2\text{(NH}_2\text{)C}_6\text{H}_3\text{—AsO(OH)}_2$	285.92	0.024
3,5-Dinitro-4-hydroxy-benzenearsonic acid	$\text{HO(NO}_2\text{)}_2\text{C}_6\text{H}_3\text{—AsO(OH)}_2$	308.00	0.024
4-Methylbenzenearsonic acid	$\text{CH}_3\text{—C}_6\text{H}_4\text{—AsO(OH)}_2$	216.03	0.024
3-Methyl-4-hydroxybenzenearsonic acid	$\text{CH}_3\text{(OH)C}_6\text{H}_3\text{—AsO(OH)}_2$	232.03	0.024
3-Nitroarsanilic acid	$\text{NH}_2\text{(NO}_2\text{)C}_6\text{H}_3\text{—AsO(OH)}_2$	262.03	0.024
3-Nitro-4-hydroxybenzenearsonic acid	$\text{NO}_2\text{(OH)C}_6\text{H}_3\text{—AsO(OH)}_2$	263.01	0.016
Phenylglycinearsonic acid	$\text{HO}_2\text{C—CH}_2\text{—NH—C}_6\text{H}_4\text{—AsO(OH)}_2$	275.04	0.024
Salicylarsonic acid	$\text{HO}_2\text{C(OH)C}_6\text{H}_3\text{—AsO(OH)}_2$	262.01	0.016

It is evident that the sensitivities of the reactions are not dependent on the molecular weight of the organic compound. It does appear, however, that groups such as Cl and  $\text{NO}_2$ , which increase the solubility of the arsonic acid, also tend to increase the solubility of the corresponding zirconium salt.



The zirconium salts of the compounds listed in the table are all white or yellowish-white. It has been shown, however, that by using azo derivatives of benzenearsonic acid, colored zirconium precipitates are obtained which are more readily observed, and consequently are analytically more useful.<sup>3</sup> For example, the two azoarsonic acids,



and



which are soluble in mineral acids because of the basic amino groups which they contain, react even with traces of zirconium salts in hydrochloric acid solution to form amorphous, colored precipitates. Although the azoarsonic acids are themselves colored, they can be used for the detection of zirconium, since the color of the zirconium salt is different from that of the precipitant.

The arsonic acids are more useful analytical reagents than arsenic acid, since they are capable of precipitating smaller quantities of zirconium than the latter. For example, in sulfuric acid solution many reagents fail to precipitate zirconium, since in this medium the zirconium ion concentration is diminished through the formation of the complex zirconium-sulfate anion, but even under these conditions the organic arsonic acids precipitate zirconium.

An excellent discussion of the methods for preparing the arsonic acids is included in Volume II of *Organic Reactions*.<sup>4</sup>

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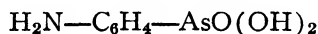
## ***o*-AMINO BENZENEARSONIC ACID**

Synonym: *o*-Aminophenylarsonic acid

$\text{C}_6\text{H}_8\text{O}_3\text{NAs}$

Mol. Wt. 217.03

Beil. Ref. XVI, 463



**Use:** Detection of scandium.

*o*-Aminobenzenearsonic acid consists of needle-like crystals. It melts at 153° C. with decomposition. It is very soluble in water and alcohol. It is also soluble in acetic acid, but only slightly soluble in ether.

**Preparation.** *o*-Nitrobenzenearsonic acid: Grind 100 g. of *o*-nitraniline under 500 ml. of 1:1 hydrochloric acid, and cool the mixture to 10° C. Diazotize with a solution of 55 g. of sodium nitrite. Stir 10-15 minutes and filter, and pour the filtrate slowly with shaking into 550 ml. of 25 per cent sodium hydroxide solution, while keeping the temperature below 0° C. Then add the alkaline solution to 135 g. of sodium arsenite dissolved in 1250 ml. of water, and heat the mixture to 60-70° C. for 1.5-2 hours. Avoid overheating. Acidify the mixture

with a slight excess of acetic acid, treat with decolorizing charcoal, and filter. Add hydrochloric acid to the filtrate until strongly acid to Congo red. Chill thoroughly to crystallize the nitro compound as a yellow powder. Recrystallize from water.

*o*-Aminobenzenearsonic acid: Dissolve 300 g. of ferrous sulfate in 900 ml. of warm water, chill thoroughly, and transfer to a wide-mouth bottle fitted with a rubber stopper. Add 25 per cent sodium hydroxide until the mixture is strongly alkaline to litmus after shaking. Dissolve 40 g. of *o*-nitrobenzenearsonic acid in dilute sodium hydroxide, and add immediately to the alkaline ferrous sulfate mixture. Shake vigorously for 5 minutes. Filter on a Buchner funnel, and wash with water. Acidify the alkaline filtrate and washings with hydrochloric acid, warm, and treat with a concentrated solution of barium chloride until the sulfate is completely precipitated. Avoid an excess of barium chloride. Make the filtrate slightly alkaline, and evaporate to a small volume in vacuum. Filter off the precipitate of sodium chloride, and wash with a saturated solution of sodium chloride. The volume of the filtrate should be about 200 ml. Treat with hydrochloric acid until Congo red paper just begins to turn. The reagent crystallizes as a mass of needles. Chill thoroughly, filter, and wash with ice water.<sup>1</sup>

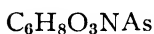
**Detection of scandium.** An intense yellow color is obtained when solutions of *o*-aminobenzenearsonic acid and salicylaldehyde are added to an acetic acid solution containing scandium. The sensitivity of this reaction is 1:2,000,000. Other elements of Group III of the periodic table do not give this color, but a color reaction is obtained with all elements precipitated by the arsonic acids. Titanium and thorium give colors which are as bright as those obtained with scandium.

Only *o*-aminoarsonic acids and *o*-hydroxyaldehydes yield Schiff bases, which are capable of giving the scandium reaction.<sup>2</sup>

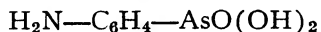
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## ARSANILIC ACID

Synonym: *p*-Aminophenylarsonic acid, atoxylic acid



Mol. Wt. 217.04      Beil. Ref. XVI, 878(466)



**Use:** Detection of ammonia and cerium.

Determination of zirconium.

Arsanilic acid is a white crystalline powder. It melts at 232° C., and is very poisonous. It is slightly soluble in cold water, alcohol, and acetic acid. It is soluble in hot water, amyl alcohol, ether, solutions of alkali carbonates, and concentrated mineral acids, but is insoluble in acetone, benzene, chloroform, and dilute mineral acids.

**Preparation:** Place 103.5 g. of arsenic acid (80-85 per cent) in a large evaporating dish, and add 80 ml. of aniline with rapid stirring. Transfer the

solid which forms to a round-bottom flask equipped with a thermometer reaching to the bottom of the flask, and fitted with a reflux condenser. Add an additional 80 ml. of aniline, and heat on an oil bath at 155-160° C. for several hours, shaking occasionally. Pour the mixture into 70 ml. of water, and wash out the flask with a portion of a previously prepared solution containing 33 g. of sodium hydroxide in 140 ml. of water, and add the washings to the reaction mixture. Then add the remainder of the alkali solution, shake well, and cool with running water. Separate the lower layer, while it is still warm, by means of a separatory funnel that has also been warmed to prevent the separation of sodium arsanilate. Treat with decolorizing charcoal and filter. Acidify the filtrate with concentrated hydrochloric acid to a yellow color with tetrabromophenolsulfonphthalein. Do not pass the end-point during the addition of the acid. Scratch the side of the flask, and allow to stand overnight. Filter, digest with 35 ml. of alcohol, filter, and recrystallize the product from 250 ml. of boiling water to which a little Norite has been added.<sup>1</sup>

**Determination of zirconium.** Arsanilic acid gives a voluminous white precipitate with zirconium ions in solutions which are 0.5 N in hydrochloric or sulfuric acid. Precipitation is quantitative, and can be used for the gravimetric determination of zirconium.<sup>2,3</sup>

**Procedure.** Dilute a sulfuric acid solution of zirconium to 200 ml. and add 1 g. of arsanilic acid for each 0.04 g. of  $ZrO_2$ . Boil the mixture for 10 minutes, and allow to stand for several hours until cold. Wash the precipitate by decantation with 150 ml. of 0.5 N sulfuric acid, used in three portions. Transfer to a filter, and finally wash with 100 ml. of water. Dry and ignite, first in air, and then in hydrogen, and then in air again, and finally weigh as  $ZrO_2$ .

This method has proved satisfactory for solutions containing up to 4 N sulfuric acid. Most other ions do not interfere. In solutions 4 N in sulfuric acid, zirconium can be determined in the presence of nickel, cobalt, aluminum, chromium, zinc, manganese, copper, and magnesium. Iron and titanium may interfere and must be removed. Iron is best removed by converting to ferric chloride, and shaking the 6 N hydrochloric acid solution with ether. Titanium is removed by treating with ammonium hydroxide and hydrogen peroxide.

**Detection of cerium.** A 5 per cent solution of sodium arsanilate reacts with ceric ions in dilute sulfuric acid solution to give a deep reddish-brown color.<sup>4</sup> This reaction is very sensitive and may be used for the detection of cerium, although it is not suitable for the colorimetric determination of this metal.

Zirconium interferes with the above reaction by forming a white precipitate with the reagent, and the color of chromium and cobalt solutions prevents the observation of the color of the cerium reaction product. Thorium may also precipitate slightly, and fluorides, too, may interfere.

The sensitivity of the cerium reaction is 1:100,000, but in the presence of cupric, ferric, uranyl, and tungstate ions, the sensitivity is only 1:50,000.

**Detection of ammonia.** Ammonia reacts with diazotized sodium arsanilate to give an intense yellow color. This reaction has been used by Korenman<sup>5</sup> to detect ammonia in air.

**Procedure.** To 3-5 ml. of a saturated aqueous solution of sodium arsanilate, add a few crystals of sodium nitrite, and not more than 2 drops of 2 N hydrochloric acid. Impregnate filter paper with this solution, and expose to air, or other gas to be tested. The test paper is almost colorless, but in the presence of ammonia it turns an intense yellow.

As little as 0.018 mg. of ammonia per liter of air can be detected in this manner.

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## BENZENEARSONIC ACID

Synonym: Phenylarsonic acid

$C_6H_7O_3As$

Mol. Wt. 202.03

Beil. Ref. XVI, 868



**Use:** Determination of bismuth, columbium, tantalum, thorium, tin and zirconium.

Detection of columbium, tantalum and tin.

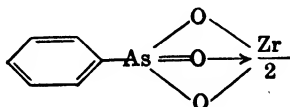
Separation of thorium, titanium and zirconium.

Benzeneearsonic acid is a white crystalline powder. It melts at 158-162° C. with decomposition. It is soluble in 40 parts of water and in 50 parts of alcohol, but it is insoluble in chloroform.

**Preparation:** In a 25-liter copper vessel, fitted with a mechanical stirrer, place 4 liters of water, 2 kg. anhydrous sodium carbonate, 1 kg. technical arsenious oxide and 45 g. of crystalline copper sulfate. Cool the mixture to 15° C. with several streams of water, start the stirrer running, and add a solution prepared as follows (prepare and add in four portions): In a 4-liter flask, place a mixture of 186 g. of aniline, 400 ml. of concentrated hydrochloric acid, and 1 liter of water, and then add sufficient ice to bring the total volume to 3 liters. Diazotize with a concentrated solution of 140 g. of sodium nitrite. Approximately 3 hours are required to run 4 of these solutions into the arsenite mixture, while maintaining the temperature at 15° C. The addition of 10 ml. of benzene controls excessive foaming. Stir the mixture for 30 minutes after all the diazo compound has been added, and then filter and concentrate the filtrate to 5 liters. Add concentrated hydrochloric acid in small portions and filter off the tarry material which separates. Continue the addition of acid until the filtrate is a clear pale yellow. At this point precipitate benzeneearsonic acid by the addition of more hydrochloric acid, being careful to avoid excess of acid.

Cool the neutralized mixture, filter, and wash with a little distilled water. Purify the product by crystallizing from water.<sup>1</sup>

**Determination of zirconium.** Benzenearsonic acid reacts with zirconium in the presence of considerable mineral acid to form a very insoluble compound having the following composition.<sup>2</sup>



The precipitation of zirconium with benzenearsonic acid affords an accurate and convenient method of determining zirconium in steel. The following procedure has been suggested by Klinger.<sup>3</sup>

**Procedure.** Remove most of the iron as ferric chloride by repeated extraction of a hydrochloric acid solution of the sample with ether. Dilute the aqueous solution to 500 ml. and add 50 ml. of concentrated hydrochloric acid. If titanium is present, add 50 ml. of 3 per cent hydrogen peroxide. Then precipitate the zirconium by adding a 2.5 per cent solution of the reagent. Ignite the precipitate in a platinum crucible, treat with hydrogen fluoride and sulfuric acid, ignite again, and weigh as  $\text{ZrO}_2$ .

The solution in which precipitation takes place should be freed from silicon and tungsten in the usual manner. The insoluble tungstic oxide should be digested with ammonium hydroxide solution, and the insoluble residue digested with hydrochloric acid to remove any zirconium that may have been co-precipitated.

Most of the methods previously described for separating and determining zirconium in the presence of iron are difficult and time consuming when many other ions are present. The use of benzenearsonic acid as the precipitating agent, however, makes possible a determination of zirconium without other elements being precipitated except the closely allied and the always-present hafnium.

If very much iron is present, the precipitation should be carried out a second time, and this is done after dissolving the first precipitate in 18 N sulfuric acid. The quantity of benzenearsonic acid required to precipitate 50 mg. of zirconium is 250 mg.<sup>4</sup>

Hackl<sup>5</sup> has studied the sensitivity of the zirconium precipitation and reports a turbidity with the reagent when 3-4 mg. of  $\text{ZrO}_2$  as  $\text{Zr}(\text{SO}_4)_2$  is present in 100 ml. of solution. Rice, Fogg and James<sup>2</sup> have described procedures for determining zirconium in the presence of the following: uranium, bismuth, copper, iron, aluminum, titanium, thorium, the cerium group, potassium, manganese, cobalt, nickel, zinc, beryllium and phosphoric acid.

**Detection of tin.** Benzenearsonic acid (and other arsonic acids) precipitate stannic tin quantitatively from solutions of stannic chloride. This reaction is used for the detection and the determination of tin. Precipitation occurs only with a relatively high concentration of the reagent at low acidity of the solution, and in the absence of organic complex-forming substances. Stannic tin, pres-

ent in the form of stannyl chloride  $\text{Sn}_5\text{O}_5\text{Cl}_2(\text{OH})_2$ , is completely precipitated by benzenearsonic acid in the presence of considerable acid and organic compounds which form tin complexes.<sup>6</sup>

Tin may be detected in a systematic scheme of qualitative analysis with the aid of benzenearsonic acid by using the following procedure:<sup>7</sup>

**Procedure.** Digest the precipitated sulfides of arsenic, antimony and tin with concentrated hydrochloric acid, and dilute somewhat with water. Filter, and to 5 ml. of the hot filtrate add 10 ml. of a solution of benzenearsonic acid. If tin is present, a turbidity or precipitate appears.

The solution to be analyzed must be hot since otherwise antimony oxychloride may be precipitated.

Since precipitation of stannic tin with benzenearsonic acid is quantitative, this reaction affords a useful method for the gravimetric determination of tin. Conditions must, however, be rather carefully controlled to obtain satisfactory results. The tin precipitate may be contaminated by many other ions which are present in the solution from which the precipitation is made.<sup>6,8</sup>

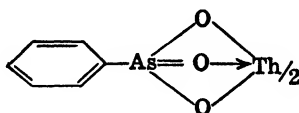
The following method for the determination of tin has been used by Knapper, Craig, and Chandlee:<sup>9</sup>

**Procedure.** Treat the sample to be analyzed containing 0.1 g. of tin with 10 ml. of 1:1 nitric acid, and heat until the metals are oxidized and the excess acid removed. Then add hydrochloric acid until solution is complete, and dilute to 150-200 ml. The acid content of this solution should be 5 per cent hydrochloric acid or 7.5 per cent sulfuric acid by volume. To the hot solution add a saturated aqueous solution of benzenearsonic acid until precipitation is complete. Filter, wash the filtrate with a 4 per cent ammonium nitrate solution, and ignite at 1075-1100° C., and weigh as  $\text{SnO}_2$

Using this method, tin may be separated from copper, zinc, lead, nickel, iron, cadmium, aluminum and bismuth, but not from zirconium or thorium.

Suirokonskii and Pil'nik<sup>10</sup> have used the method of Knapper and co-workers for determining tin in tin ores. Mack and Hecht<sup>11</sup> have attempted to determine smaller quantities of tin in the presence of other elements likely to be associated with tin by precipitation with benzenearsonic acid, but have reported that they were unable to obtain satisfactory results.

**Determination of thorium.** Benzenearsonic acid reacts with thorium salts in fairly concentrated solutions of acetic acid to form an insoluble compound of the following composition:



Rice, Fogg and James<sup>2,15,16</sup> have used this reaction for determining thorium in the presence of the rare earths and monazite sand.

**Procedure.** Digest 25 g. of monazite sand with 50 ml. of concentrated sulfuric acid for 12 hours on a hot plate. Cool and slowly add the mixture to 500 ml. of cold water and stir. Filter, and dilute the filtrate to 1 liter. To 100 ml. of this solution, add 15 ml. of concentrated nitric acid, and pour this mixture into a hot solution containing approximately 10 g. of oxalic acid. Allow to stand for a short time and filter off the precipitate. Wash and decompose the precipitate by boiling with concentrated nitric acid. When the volume is about 15 ml., add a hot solution containing about 10 g. (an excess) of oxalic acid and dilute to 200 ml. Filter, again dissolve the precipitate in concentrated nitric acid, and evaporate almost to dryness. Treat the residue with about 300 ml. of water, and reduce ceric cerium by the careful addition of sulfurous acid. Heat to boiling, add 30 ml. of 10 per cent benzenearsonic acid solution and 75 ml. of acetic acid. Then add slowly a concentrated solution of ammonium acetate until precipitation is complete. Digest for 10 minutes on a hot plate and filter. Wash the precipitate and dissolve in 30 ml. of 1:1 hydrochloric acid. Dilute to 300 ml. and again treat with a little sulfurous acid. Reprecipitate the thorium by adding a few ml. of the benzenearsonic acid solution, 75 ml. of acetic acid, and sufficient ammonium acetate to insure complete precipitation. Filter, dissolve the precipitate in 30 ml. of 1:1 hydrochloric acid, and treat the solution with 5 g. of oxalic acid and dilute to 200 ml. Allow to stand for 12 hours. Filter off the oxalate, wash, ignite and weigh.

Grundmann<sup>17</sup> has used benzenearsonic acid to precipitate thorium, along with zirconium, hafnium and titanium from a dilute acetic acid solution. He then dissolved the washed precipitate in hydrochloric acid and finally precipitated thorium with oxalic acid.

Wenger and Duckert<sup>18</sup> recommend the use of this reagent for the detection of thorium. The reaction is sensitive to 20 $\gamma$  of thorium. Cerium and zirconium react similarly.

**Detection and determination of columbium and tantalum.** Columbium and tantalum are precipitated by benzenearsonic acid by a procedure similar to that employed for precipitating zirconium and tin.<sup>12,19</sup> Columbium and tantalum salts are precipitated from a solution strongly acid with tartaric acid in the absence of zinc, zirconium and titanium. This reaction may be used to detect 2 $\gamma$  of columbium or tantalum in 1 ml. of solution. Interference by titanium and zirconium may be eliminated by removal by means of pyrogallol. The precipitation of tantalum and columbium with benzenearsonic acid from a solution containing a large excess of tartaric acid has been studied by Alimarin and Frid<sup>13</sup> as a possible method for the determination of columbium and tantalum. A satisfactory method has been reported for the determination of these metals in minerals and ores, even in the presence of aluminum, iron, uranium, vanadium, manganese and the rare earths.<sup>20</sup>

**Separation of gallium.** Benzenearsonic acid may be used instead of cupferon to precipitate titanium in the presence of gallium, but the procedure is more complicated and hence less useful. Thorium and zirconium may also be separated from gallium by means of a similar procedure.<sup>14</sup>

**Determination of bismuth.** Bismuth is quantitatively precipitated with benzenearsonic acid as  $\text{BiC}_6\text{H}_5\text{AsO}_4$  from an acetic acid solution buffered with sodium acetate or ammonium acetate. The pH is 5.1-5.3. Anions like citrate or oxalate which form complexes with bismuth ions must be absent. Fluoride, chloride and phosphate must also be absent. Since benzenearsonic acid also precipitates iron, aluminum, beryllium, uranium and titanium, these metals must be absent. Chromium causes contamination, and the method is unsatisfactory if zinc, manganese, or antimony is present. Mercury must be present in the mercuric state. Bismuth can be separated from silver, copper, cadmium, cobalt, nickel, mercury and lead in the presence of potassium cyanide. Benzenearsonic acid also precipitates zirconium, thorium and tin from acidic solutions under conditions such that no bismuth is precipitated. After removing these precipitates by filtration, bismuth is determined in the filtrate by neutralization.<sup>21,22</sup>

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### ***p*-n-BUTYLBENZENEARSONIC ACID**

Synonym: *p*-n-Butylphenylarsonic acid

$\text{C}_{10}\text{H}_{15}\text{O}_3\text{As}$

Mol. Wt. 258.13



**Use:** Determination of iron.



**Preparation: Butylbenzene:** Place 225 g. of sodium (1 mm. cubes) in a 3-liter flask, fit with a stirrer, dropping funnel, condenser and thermometer, and cover with a minimum amount of ether which has been dried over sodium. Mix 600 g. of butylbromide and 600 g. of bromobenzene and add the mixture slowly to the sodium by means of a dropping funnel. The time for the addition is about 9 hours. Allow the mixture to stand for 2 days and decant the liquid from the blue colored residue. Add 150 ml. of alcohol to the flask and heat on a steam-bath until the sodium has entirely reacted, and then cautiously add water to dissolve the sodium bromide. Separate the upper oily layer, and add to the liquid originally decanted from the solid. Wash the combined oils with water and dry over calcium chloride. Separate the butylbenzene by fractional distillation, collecting the fraction boiling at 160-185° C. Redistil with a fractionating column, and retain the fraction boiling between 179-182° C.

*Nitration of butylbenzene:* Add 50 g. of butylbenzene slowly to 50 g. of concentrated sulfuric acid at 0° C., and to this mixture add a nitrating mixture consisting of 37.5 g. of concentrated nitric acid and 78.7 g. of concentrated sulfuric acid with stirring. Keep the temperature at 0° C. at all times with an ice bath. After the nitrating mixture has been added, stir for 30 minutes at a temperature below 5° C. Pour the mixture into a large beaker containing 200 g. of ice and separate the orange colored oil, and then extract the aqueous layer with benzene. Combine the oil and benzene extract and wash with a 10 per cent sodium carbonate solution until the acid is neutralized and then wash with water. Dry the oil over anhydrous sodium sulfate. Separate the benzene by distillation, and collect the *p*-nitrobutylbenzene, which boils at 144-148° C. at 12 mm. pressure.

*Reduction of the p-nitrobutylbenzene.* Place 40 ml. of water in a 1-liter flask which is fitted with a dropping funnel, condenser and stirrer, and add 80 g. of fine iron powder with stirring to prevent caking. Heat to 100° C. with stirring, and cautiously add 30 ml. of 1:1 hydrochloric acid. Keep the temperature at 100° C. and add 70 g. of *p*-nitrobutylbenzene from a dropping funnel with vigorous stirring. When the reaction is completed, cool and make strongly alkaline with 160 ml. of 25 per cent sodium hydroxide. Filter the alkaline sludge which remains in the flask, separate the oil which is obtained, extract the aqueous layer with benzene and wash the residue with benzene. Combine the extracts and the oil and dry over solid sodium hydroxide. Remove the benzene by distillation and recover the *p*-aminobutylbenzene by distilling under reduced pressure.

*Diazotization and arsonation of p-amino-n-butylbenzene:* Dissolve 15 g. of *p*-amino-*n*-butylbenzene in 200 ml. of water and 22.4 ml. of concentrated hydrochloric acid. Cool to 0° C. with ice and add 95 ml. of 1 N sodium nitrite solution slowly from a dropping funnel. The arsonation of the diazotized solution is carried out immediately. Dissolve 19.5 g. of sodium arsenite ( $\text{NaAsO}_2$ ) in 150 ml. of water and to this add a solution prepared by dissolving 2 g. of copper sulfate in 25 ml. of water. Now add the green sodium arsenite-copper sulfate mixture to the diazotized solution with stirring. Allow the mixture to warm to

room temperature, and add 40 ml. of 6 N sodium hydroxide slowly with stirring. Continue the stirring for 2 hours. Then heat on a steam bath to 65° C. for 20 minutes with stirring. Filter off the brown residue, and evaporate the solution to 300 ml. Add a little animal charcoal, and filter while still hot, and cool to 5° C. Carefully acidify the cold filtrate with 6 N hydrochloric acid. Purify the crystalline solid which forms by recrystallization from hot water.<sup>1</sup>

**Determination of iron.** A white flocculent precipitate is formed when a 0.75 per cent solution of *p*-*n*-butylbenzenearsonic acid is added to an acid solution containing ferric salts. The temperature should be 80-90° C. and the acidity not greater than 0.4 N in mineral acid. The precipitate may be filtered after standing overnight, washed with warm 0.02 N hydrochloric acid, and then with water until free from chlorides, ignited strongly, and weighed as Fe<sub>2</sub>O<sub>3</sub>.

Nickel, zinc, cobalt, manganese, copper, cadmium, potassium, aluminum, magnesium, calcium, beryllium, lanthanum, erbium, neodymium, chromate, thallium, and vanadate do not interfere with this determination. Iron cannot, however, be determined by this method in the presence of zirconium, tin, titanium, thorium, uranium, or cerium, or in the presence of anions which form complexes with iron, such as fluoride, phosphate, tartrate and citrate.<sup>2</sup>

1. Thesis of W. L. Evers, Northwestern Univ.

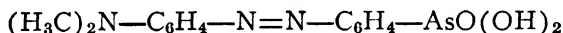
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### ***p*-DIMETHYLAMINOAZOBENZENEARSONIC ACID**

C<sub>14</sub>H<sub>16</sub>O<sub>3</sub>N<sub>3</sub>As

Mol. Wt. 349.20

Beil Ref. XVI, 885



**Use:** Detection of fluoride and zirconium.

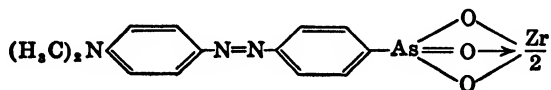
Determination of zirconium.

*p*-Dimethylaminoazobenzeneearsonic acid is a reddish powder, which is easily soluble in acids and alkalis.

**Preparation:** Dissolve 22 g. of arsanilic acid in 200 ml. of hydrochloric acid, and diazotize in the usual manner with the calculated quantity of sodium nitrite. To the diazotized mixture, add a solution of 12 g. of dimethylaniline in 2 N hydrochloric acid. Allow the mixture to stand at 0° C. for one hour, and then precipitate the reagent with sodium acetate. Purify by recrystallizing the precipitate from hot 2 N hydrochloric acid. The compound is obtained as the hydrochloride.<sup>1</sup>

**Detection of zirconium.** Like arsenic acid and its organic derivatives, such as benzenearsonic acid, *p*-dimethylaminoazobenzeneearsonic acid yields a sparingly soluble compound when added to acid solutions of zirconium salts. Unlike some of the other arsonic acids, however, *p*-dimethylaminoazobenzeneearsonic acid yields a colored insoluble zirconium salt, and this is a marked advantage when the compound is used as an analytical reagent for zirconium.<sup>1-3</sup> Another

advantage in the use of *p*-dimethylaminoazobenzenearsonic acid lies in the ease with which it may be prepared. The zirconium salt of this derivative of arsenic acid forms in an acid solution as a brown precipitate which has the following composition:



When formed in a spot test on filter paper, the brown precipitate remains in the pores of the paper as a characteristic lake color, whereas the excess of the colored reagent may be washed away with dilute acid.

**Reagent.** Dissolve 0.1 g. of *p*-dimethylaminoazobenzenearsonic acid in 100 ml. of alcohol containing 5 ml. of concentrated hydrochloric acid. Impregnate filter paper with this solution and allow to dry.

**Procedure.** Place a drop of the acid solution to be tested on the reagent paper. A brown stain appears at once if large amounts of zirconium are present. To make the color of the zirconium compound more clearly visible, soak the paper for a short time in 2 N hydrochloric acid that has been heated to 50-60° C. In this way the excess reagent, which may mask the color of the zirconium compound, is removed. As little as 0.1γ of zirconium can be detected in this way. The concentration limit is 1:500,000.

Sulfuric acid causes a marked reduction in the sensitivity of this test if present in concentrations greater than normal. This is due to the formation of complex zirconium-sulfuric acids. Fluorides, phosphates and organic acids which yield precipitates or stable soluble complexes with zirconium salts also prevent or reduce the sensitivity of the above test. Pentavalent antimony reacts with the reagent to produce a brown coloration similar to that formed with zirconium salts, but this disappears after a few minutes' treatment with hydrochloric acid. As little as 0.25γ of zirconium may be detected in the presence of 1,000 times as much antimony. Trivalent antimony may give a slight, colored stain with the reagent, but this disappears immediately on immersion in the hydrochloric acid solution. Thorium salts also react like zirconium, but the color formed by these compounds also disappears immediately when treated with hydrochloric acid; consequently, 0.2γ of zirconium may be detected in the presence of 2,500 times as much thorium. Gold salts, if present in large amounts, give a violet coloration with the reagent, but this, too, disappears at once when treated with hydrochloric acid.

**Detection of zirconium in the presence of molybdenum and tungsten.** Like zirconium, molybdates and tungstates react with *p*-dimethylaminoazobenzenearsonic acid to yield reddish-brown colorations which are stable in 2 N hydrochloric acid. By converting the molybdates and tungstates into the peracids by the addition of hydrogen peroxide, however, these compounds give little or no reaction with the reagent, and consequently may be rendered harmless in carrying out the test for zirconium. The following procedure is to be used for detecting zirconium in the presence of molybdenum and tungsten:

**Procedure.** Mix 3 drops of the solution to be tested, which should not contain more than 1 per cent of molybdenum or 0.5 per cent of tungsten, on a spot plate with a drop of a mixture of concentrated hydrochloric acid and 30 per cent hydrogen peroxide. Place a drop of this mixture on the reagent paper described in the above procedure. The paper is then placed in the warm acid bath as described above. A red fleck appears at the center of the moist spot and this soon disappears. When zirconium is present, however, a brown ring of the zirconium salt appears about the fleck, and at the same time some of the stain caused by tungsten, and to a slight extent also by molybdenum, remains on the paper. By this procedure as little as 0.5 $\gamma$  of zirconium may be detected in the presence of 1,000 times as much molybdenum or 500 times as much tungsten.

It appears that zirconium induces the precipitation of tungsten and molybdenum compounds, but due to the separation of the stains on the paper as a brown ring with a red center, very small quantities of zirconium may be detected in the presence of large quantities of tungsten and molybdenum. If the concentration of tungsten or molybdenum is small, the brown ring of the zirconium compound alone is observed.

**Detection of zirconium in the presence of titanium and cerium.** Titanium salts may also interfere with the zirconium test, but like molybdates and tungstates, they may be converted with hydrogen peroxide into the peracid, which does not give a color with the reagent. Tetravalent cerium salts interfere by destroying the reagent, and causing a yellow color, but they are easily reduced to cerous salts by the addition of hydrogen peroxide and thus rendered harmless. The following procedure is used for testing for zirconium in the presence of titanium and cerium.

**Procedure.** Place 2-3 drops of the solution to be tested on a spot plate and add a drop of concentrated hydrochloric acid and a drop of 30 per cent hydrogen peroxide. Then place a drop of this mixture on the reagent paper described above, and immerse for a short time in hydrochloric acid. A brown ring or fleck appears depending on the amount of zirconium present. As little as 1 $\gamma$  of zirconium can be detected in the presence of 500 times as much titanium.

**Detection of zirconium in the presence of tin.** Stannic salts in high concentrations react with *p*-dimethylaminoazobenzeneearsonic acid to yield a brown precipitate. In the presence of concentrated acids, however, the brown compound does not form. The following procedure is used to detect zirconium in the presence of tin.

**Procedure.** Place 3 drops of the solution to be tested, which should not contain more than 0.1 per cent of tin, on a spot plate and mix with a drop of concentrated hydrochloric acid. Place a drop of this mixture on the reagent paper described above and immerse as usual in a solution of warm dilute hydrochloric acid. In the presence of zirconium, a more or less intense brown ring or fleck appears. A slight reddish coloration may appear in the absence of zirconium if tin is present. As little as 0.2 $\gamma$  of zirconium may be detected by this procedure in the presence of 250 times as much tin.

**Determination of zirconium.** The zirconium salt of *p*-dimethylaminoazobenzenearsonic acid is easily decomposed by an alkali hydroxide to form  $\text{Zr}(\text{OH})_4$  and a water soluble salt of the reagent. The colored solution thus formed may be used for a colorimetric comparison with standard solutions of the reagent. In this way quantities of zirconium ranging from 0.02 to 1.0 mg. may be determined in the presence of titanium, thorium, cerium, iron and uranium.<sup>3,4</sup> The following procedure for determining zirconium in steel is described by Hayes and Jones.<sup>5</sup>

**Reagent.** Dissolve 0.25 g. of *p*-dimethylaminoazobenzenearsonic acid in 10 ml. of concentrated hydrochloric acid and dilute with ethyl alcohol to 250 ml.

**Procedure.** Dissolve 1 g. of the sample to be analyzed in 50 ml. of 1:1 hydrochloric acid. When solution is complete, dilute to 75 ml. and filter. Save

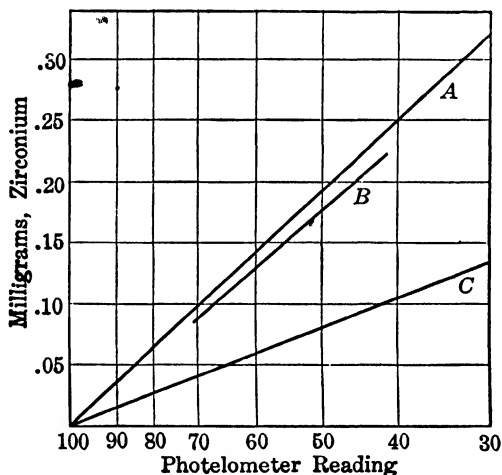


FIG. 3.

this filtrate for a later step in the procedure. Wash the residue three times with hot water, three times with hot 1:1 hydrochloric acid, and three times with hot water. Ignite the paper and residue in a platinum crucible, fuse the ash with a small quantity of potassium acid sulfate, and dissolve the cooled melt by heating the crucible and melt in a beaker containing 100 ml. of water and a few drops of sulfuric acid. Remove the crucible, wash well with hot water, and to the solution containing the dissolved melt, add two drops of methyl orange indicator solution, and a slight excess of ammonium hydroxide. Boil for one minute, filter, and wash the precipitate with cold water. Place the filter and contents back into the beaker, add 50 ml. of 1:1 hydrochloric acid, and heat to boiling. Boil for a minute and filter into the original filtrate saved from the first filtration. Wash well with hot water, and transfer the filtrate to a 500-ml. volumetric flask. Dilute to the mark with distilled water.

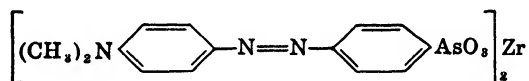
Mix well and transfer a 50-ml. aliquot to a 250-ml. beaker. Heat to boiling, add 15 ml. of the reagent solution, cover with a watch glass, and then boil for

one minute. Allow to stand at room temperature for at least 30 minutes, and then filter through three close-texture filter papers. Wash the excess reagent from the paper and the precipitate with 1:100 hydrochloric acid, and when the washings come through colorless, place the funnel containing the paper and precipitate in the neck of a 100-ml. volumetric flask, and remove the reagent which is combined with the zirconium by washing 3-4 times with 1:3 ammonium hydroxide. Dilute to volume with distilled water, mix well, and filter through cotton into the absorption cell of a photometer. The zirconium content is obtained from the curve prepared by measuring the absorption of standard zirconium solutions. A blue filter is used in reading the photometer.

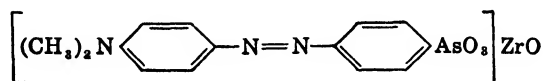
This determination can be made without preliminary separation of the zirconium from iron and other elements, such as manganese, silicon, and chromium. In the presence of these elements, however, standardization against a similar steel of known zirconium content is necessary.

When the milligrams of zirconium are plotted against the photometer readings (Cenco-Sheard-Sanford type) on semi-log paper, curves similar to those shown in Figure 3 are obtained.

When no considerable quantity of other metals is present, and the solution to be precipitated contains more than 5γ in 10 ml. or less of 2 N hydrochloric acid, line C is obtained. The precipitate formed under these conditions probably consists of



When solutions contain the same amount of zirconium in 50 ml. of 2 N hydrochloric acid, curve B is obtained. The precipitate in this case probably consists largely of



Line A, which is the one used in the above procedure, is obtained by precipitating the zirconium from 50 ml. of a solution containing 0.1 g. of steel, which is analyzed by the selenious acid method.

The accuracy of the above method may be improved somewhat by a preliminary separation of zirconium by the use of a mercury cathode, or some other suitable method. This treatment makes possible the use of line C, which gives about twice as many scale divisions for the same quantity of zirconium.

The method of Hayes and Jones is recommended, since the entire analysis requires less than 2 hours, and the results are said to be within 0.005 per cent of the weight of the sample as compared with those values obtained with the selenious acid method. Titanium tends to interfere for reasons described in the detection of zirconium, but this interference is prevented by adding a little hydrogen peroxide before precipitating the zirconium compound. The quantity of titanium, however, must not exceed 10 times that of the zirconium present.

**Detection of fluorides.** Soluble fluorides react with the brown insoluble zirconium compound formed by the action of *p*-dimethylaminoazobenzeneearsonic acid on acid solutions of zirconium salts to form the colorless  $(ZrF_6)^-$  and set free *p*-dimethylaminoazobenzeneearsonic acid, which is red in color. Thus if a drop of an acid fluoride solution is placed on filter paper which has been impregnated with the zirconiumazoarsonate, the color changes from brown to red. This reaction has been used by Feigl and Rajmann<sup>6</sup> as a sensitive test for fluoride.

**Reagent.** Prepare a test paper as follows: Immerse a strip of filter paper (Schleicher & Schull No. 589) for a few minutes in a 0.025 per cent solution of *p*-dimethylaminoazobenzeneearsonic acid in a mixture composed of 9 parts of alcohol and 1 part of concentrated hydrochloric acid. Remove the paper and allow to dry in air, and then place in a 0.01 per cent zirconium oxychloride solution in 1 N hydrochloric acid. By this treatment the bright-red paper is colored brown. Allow the paper to remain in the zirconium oxychloride solution for 10 minutes. Wash the paper at 5-minute intervals with both cold and warm (50° C.) 2 N hydrochloric acid, then with water, and finally with alcohol and ether, and then dry in a vacuum desiccator.

**Procedure.** Place 3 drops of the neutral or alkaline solution to be tested on a spot plate and mix with a drop of 2 N hydrochloric acid. Transfer a drop of this mixture to the light brown reagent paper. If fluoride is present, the center of the moist spot appears colorless, and this colorless zone is surrounded by a red circle of the liberated reagent. By this method 0.25 $\gamma$  of fluoride can be detected. The concentration limit is 1:200,000.

Various ions interfere with this reaction. This interference is essentially the same as that described above in the discussion of the detection of zirconium. Anions which form insoluble or stable but soluble complex compounds with zirconium, such as phosphates, arsenates, thiosulfates and sulfates interfere. Perhaps the most satisfactory method of carrying out the test in the presence of interfering substances is based upon the conversion of the fluoride into hydrofluoric acid before applying the final test. This procedure also possesses the distinct advantage that it can be conveniently applied to the analysis of insoluble compounds and minerals. The procedure is as follows:

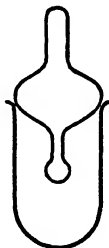


FIG. 4.

**Procedure.** Place a few particles of the solid on the bottom of the apparatus shown in Figure 4, and then add a drop of concentrated sulfuric acid. Place a drop of dilute hydrochloric acid on the knob of the stopper (see figure) and close the vessel. Warm the apparatus over an asbestos plate to hasten the formation of the hydrofluoric acid. It is important that the mixture not be heated too long, since appreciable quantities of sulfuric acid may be volatilized and thus interfere with the fluoride detection. A convenient method of regulating the heating period is to add a crystal of tartaric acid to the mixture and to discontinue the heating when the contents of the apparatus begin to char. After heating for 1-2 minutes, place the drop on the knob of the apparatus on a strip of filter paper which has been impregnated with the zirconium-*p*-dimethylaminoazobenzeneearsonic compound as described above. If a solution of a fluoride is to be treated in this manner for the elimination of interfering substances, evaporate a few drops of the liquid to dryness, and place the residue in the apparatus and proceed as described above. By this method as little as 0.2γ of fluoride may be detected in the presence of 80,000 times as much foreign substances.

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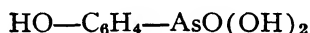
### *p*-HYDROXYPHENYLARSONIC ACID

Synonym: *p*-Hydroxybenzeneearsonic acid

$C_6H_7O_4As$

Mol. Wt. 218.03

Beil. Ref. XVI, 874



**Use:** Detection and determination of titanium and zirconium.

*p*-Hydroxyphenylarsonic acid is a white odorless powder. It melts at 175-180° C. with decomposition. It is very soluble in water and is also soluble in alcohol.

**Preparation:** *p*-Hydroxyphenylarsonic acid can be prepared by the arsonation of phenol by the method of Christiansen and Norton.<sup>8</sup>

Boil 720 g. of sirupy arsenic acid (75-80 per cent) until the temperature of the acid is 150° C. About 120 g. of water is removed to leave approximately 95 per cent orthoarsenic acid. Add this to 300 g. of phenol, which is contained in a 1-liter, three-necked flask that is fitted with a stirrer, a thermometer and a downward condenser. Place the flask in an oil bath and heat at once to 155-160° C. Start the stirrer.

When the temperature inside the flask reaches 140° C., the mixture begins to boil, and water passes over. Continue the distillation until 60 ml. of water



is collected. Then replace the downward condenser with a reflux condenser, and continue to boil until a total of 4 hours has elapsed from the time the contents of the flask first reached 140° C. Allow the material to cool somewhat, and pour into 4 liters of water. Stir mechanically for a short time.

Add finely ground barium hydroxide gradually and with stirring to the aqueous solution until the material is alkaline to litmus. This point is indicated by the solution turning pink. Approximately 700-800 g. of  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  is needed for the neutralization. Filter, and treat the filtrate and washings with sulfuric acid until the solution contains neither barium nor sulfate ions. Again filter, wash the precipitate thoroughly, and concentrate the filtrate to about 3 liters on a steam bath. Neutralize to litmus with sodium hydroxide, filter, evaporate until the surface of the solution is covered with crystals, and then add 2.5 volumes of alcohol. Cool in a refrigerator, filter off the crystals of sodium *p*-hydroxyphenylarsonate, wash with alcohol, and dry in an oven at 80° C.

The reagent may also be prepared as follows:

Dissolve 217 g. of *p*-aminophenylarsonic acid (arsanilic acid) in 2.5 liters of water and 81.6 ml. of concentrated sulfuric acid. Cool to 0° C. and diazotize with 70 g. of pure sodium nitrite dissolved in 350 ml. of water. Filter, heat at 70° C., and then at the boiling temperature with suspended barium carbonate until a filtered test shows no more sulfuric acid. Filter off the barium sulfate and evaporate the filtrate with the addition of 20 g. of anhydrous sodium sulfate and decolorizing charcoal. Purify by recrystallizing from 2 parts alcohol and 1 part water.<sup>1,2,7</sup>

**Determination of titanium.** *p*-Hydroxyphenylarsonic acid precipitates titanium and zirconium from aqueous solutions which are not more than 0.5 N in mineral acids. This reaction provides a convenient method for determining titanium in the presence of most other ions. For example, with this reagent titanium may be separated from iron, aluminum, zinc, cobalt, nickel, beryllium, chromium, manganese, calcium, magnesium, thallium, cerous cerium, thorium, sodium, potassium, ammonium, phosphate, molybdate, chromate, vanadate, permanganate, uranyl and vanadyl ions. Zirconium, ceric cerium and tin must be absent. Hydrogen peroxide also interferes. Only small quantities of phosphate may be present.<sup>3</sup>

The titanium precipitate apparently corresponds to the formula  $\text{Ti}(\text{C}_6\text{H}_4\text{-AsO}_3)_2$ , but satisfactory results are not obtained by weighing the titanium in this form. Upon ignition the precipitate yields  $\text{TiO}_2$ , which is recommended as the weighing form. Richter<sup>4</sup> recommends for the precipitation an acidity of about 1.2 N in hydrochloric acid after the addition of the reagent. Three or four grams of *p*-hydroxyphenylarsonic acid is sufficient for precipitating 64 mg. of  $\text{TiO}_2$ . The addition of 1 g. ammonium thiocyanate is useful in eliminating interference by iron and also in improving the filterability of the precipitate. In the presence of hydrochloric acid, some free sulfur is formed from the thiocyanate and this aids in the filtration. A large excess of thiocyanate exerts a solvent effect upon the titanium precipitate. The precipitate does not filter well and requires special paper.

The following procedure for determining titanium has been proposed by Simpson and Chandlee:<sup>3</sup>

**Procedure.** Dissolve the sample containing not more than 0.06 g. of  $\text{TiO}_2$  in hydrochloric or sulfuric acid and remove interfering metals by suitable means. The quantity of acid used should be such that the solution will be approximately, but not more than, 0.60 N in hydrochloric or 1.80 N in sulfuric acid after the reagents have been added and precipitation is complete. Dilute the mixture to about 200 ml., heat to boiling, add 2-3 g. of ammonium thiocyanate if iron is present, and finally add 100 ml. of a 4 per cent aqueous solution of *p*-hydroxyphenylarsonic acid. Boil gently for 15 minutes and cool the mixture to room temperature. Filter, wash 5-6 times with 0.25 N hydrochloric or sulfuric acid containing about 0.5 g. of *p*-hydroxyphenylarsonic acid per 100 ml. If iron is present, add 1-2 g. of ammonium thiocyanate to each 100 ml. of the wash solution. Finally, wash the precipitate 2-3 times with 2 per cent aqueous ammonium nitrate solution and ignite in the hood to  $\text{TiO}_2$ .

**Determination of zirconium.** The method of Simpson and Chandlee<sup>3</sup> may also be used for the determination of zirconium. Claassen<sup>5</sup> has subjected this method to a critical examination and finds that zirconium is completely precipitated by *p*-hydroxyphenylarsonic acid from solutions which are not more than 3 N in hydrochloric acid or 1.5 N in sulfuric acid. When the solution is acidified with sulfuric acid, however, the precipitate is very fine and difficult to filter. To convert to a weighing form, best results are obtained by heating the precipitate in a stream of hydrogen to volatilize arsenic, and then igniting in air. An incomplete precipitation of zirconium may result if too much ammonium thiocyanate is used in the procedure recommended for precipitating zirconium in the presence of iron.

A single precipitation with *p*-hydroxyphenylarsonic acid makes possible a complete separation of zirconium from copper, cadmium, vanadium, molybdenum, uranium, cerium, iron, aluminum, chromium, nickel, cobalt, zinc, magnesium, manganese, calcium, barium, strontium, and beryllium. In the presence of thorium, however, reprecipitation is necessary. Tungsten and tin are coprecipitated with zirconium, but bismuth does not interfere.

**Separation of titanium from zirconium.** Zirconium is precipitated by *p*-hydroxyphenylarsonic acid in the presence of an excess of hydrogen peroxide, while titanium is not precipitated under the same conditions. This makes possible a separation of zirconium and titanium.

**Procedure.** To a solution that is 2.5-3.0 N in sulfuric acid, add 15-20 ml. of 30 per cent hydrogen peroxide. To precipitate zirconium, use several times the usual quantity of *p*-hydroxyphenylarsonic acid. In separating 0.01 g. of  $\text{ZrO}_2$  from 0.05 g. of  $\text{TiO}_2$ , use 3 g. of *p*-hydroxyphenylarsonic acid. In washing the precipitate of the zirconium salt, add hydrogen peroxide to the wash liquid to prevent precipitation of titanium.

Generally in determining zirconium with *p*-hydroxyphenylarsonic acid, the concentration of the mineral acid should be 2.5-3.0 N. Quantities of  $\text{ZrO}_2$

ranging from 0.004 to 0.10 g. may be quantitatively separated from 10 g. of a chrome-vanadium steel in one precipitation. Phosphate interferes if present in more than small quantities.

**Detection of zirconium.** Miller and Lowe<sup>6</sup> have used *p*-hydroxyphenylarsonic acid as a reagent to confirm the presence of zirconium in a systematic scheme of analysis.

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### METHYLARSONIC ACID

Synonym: Arrhenal

$\text{CH}_3\text{O}_3\text{As}$

Mol. Wt. 139.96

Beil. Ref. IV, 613

$\text{CH}_3\text{AsO}(\text{OH})_2$

**Use:** Detection and determination of zirconium.

Methylarsonic acid is obtained as leaves by crystallizing from alcohol. It is readily soluble in water and alcohol. The acid is strongly dibasic, and is used as an analytical reagent in the form of the disodium salt. This goes under the name of *arrhenal*.

**Preparation:** Dissolve 16 g. of sublimed and washed arsenious oxide with 19.4 g. of sodium hydroxide and 10.3 ml. of methyl iodide in 190 ml. of water and 150 ml. of absolute alcohol. Allow the mixture to stand in a closed flask for 3 or 4 days. Filter the crystalline compound and wash with 50 per cent alcohol until the filtrate yields no precipitate of silver iodide when tested with silver nitrate.<sup>1</sup>

**Detection and determination of zirconium.** When a solution of zirconium chloride is treated with  $\text{Na}_2\text{CH}_3\text{AsO}_3 \cdot 6\text{H}_2\text{O}$ , a precipitate of  $\text{Zr}(\text{CH}_3\text{AsO}_3)_2$  is formed.

This reaction may be used for the detection of as little as 0.75γ of zirconium. Aluminum, chromium, nickel, cobalt, zinc, manganese, calcium and magnesium do not interfere, but if iron is present it should be removed by extracting with ether.

Since zirconium is quantitatively precipitated with methylarsonic acid, this reagent may be used for the gravimetric determination of the metal. The zirconium compound is converted into  $\text{ZrO}_2$  by heating, first in hydrogen and then in air. Zirconium may be weighed in this form. Zirconium may also be weighed as  $\text{Zr}(\text{CH}_3\text{AsO}_3)_2$  after drying at 50° C., but this does not generally yield satisfactory results.<sup>2</sup>

The precipitation of zirconium is best carried out in a solution which is not more than 0.75 N in hydrochloric acid. For 0.05 g. of zirconium, 1 g. of the reagent is added to the cold solution. This is then heated to boiling and the precipitate filtered off and washed with dilute hydrochloric acid. The following procedure is used for the determination of zirconium in ferro-zirconium:<sup>3</sup>

**Procedure.** Fuse 0.3 g. of the finely powdered sample with 4-5 g. of sodium peroxide for 10-15 minutes and allow to cool. Digest the fused mass with 300-400 ml. of hot water. If the aqueous extract is colored due to the presence of ferrate or manganate, add a little hydrogen peroxide. Filter through ashless paper and wash with hot water until the last portion of the filtrate is neutral to litmus. Dissolve the oxides from the paper by adding alternately hot 5 N hydrochloric acid and hot water. A little concentrated acid may be necessary to dissolve the last portion of the precipitate. Evaporate the solution to dryness on a water-bath, and dissolve in 50-60 ml. of 6 N hydrochloric acid. Remove the iron by repeated extractions with ether. Then evaporate the solution to a syrupy consistency on a water-bath, dissolve in 0.5 N hydrochloric acid and dilute to exactly 250 ml. Depending upon the zirconium content, use a 50-, 100- or 150-ml. aliquot. Dilute the aliquot (0.03 g. Zr) to 400 ml. with 0.5 N hydrochloric acid, and precipitate by adding 1 g. of disodium methylarsonate. Wash the precipitate with dilute hydrochloric acid and ignite in hydrogen and finally in air, and then weigh as  $\text{ZrO}_2$ .

Titanium interferes with the determination of zirconium by the above method.<sup>4</sup> A positive error results due to the retention of titanium in the precipitate, and a negative error is caused by incomplete precipitation of zirconium. If only small quantities of titanium are present, these errors may balance one another. To reduce the titanium concentration, precipitate zirconium from a hydrochloric acid solution with ammonium hydroxide in the presence of hydrogen peroxide. Titanium remains in solution as pertitanic acid. Repeat the separation if necessary.

Methylarsonic acid may be used satisfactorily for the separation of zirconium and copper. It is also useful for the analysis of aluminum-zirconium alloys, but cannot be used for the precipitation of zirconium from solutions containing tin. Methylarsonic acid does not precipitate stannic tin in 0.5 N hydrochloric acid solution, but the zirconium precipitate carries down considerable tin.

Coppieters<sup>5</sup> has studied the methylarsonic acid method and reports that it is exact, but that it is long and difficult and the reagent is not specific.

Zirconium may be determined with methylarsonic acid by means of a titrimetric procedure. This is based upon an estimation of the arsenic content of the zirconium precipitate ( $\text{Zr}(\text{CH}_3\text{AsO}_3)_2$ ). The precipitate is decomposed by heating in a Kjeldahl flask with concentrated sulfuric acid and a little potassium permanganate, and the precipitated manganese dioxide is removed by adding hydrogen peroxide. The arsenic is then distilled from the mixture as  $\text{AsCl}_3$  by heating with concentrated hydrochloric acid, potassium bromide and ferrous sulfate. The arsenic chloride in the distillate is then titrated with potassium bromate to an end-point with methyl orange.<sup>2</sup>

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3. R. Chandelle, *Bull. soc. chim. Belg.* **46**, 423-7 (1937); *C.A.* **32**, 1606 (1938).
4. R. Chandelle, *Bull. soc. chim. Belg.* **47**, 172-93 (1938); *C.A.* **32**, 5334 (1938).
5. V. Coppieters, *Ing. chim.* **22**, 179-210, 233-61 (1938); *C.A.* **33**, 9190 (1939).

## NITROPHENOLARSONIC ACID

Synonym: 2-Nitro-1-hydroxybenzene-4-arsonic acid

$C_6H_5O_6Na$ s

Mol. Wt. 263.02

Beil. Ref. XVI, (456).



**Use:** Detection of cadmium.

Nitrophenolarsonic acid consists of white needles or of amber-yellow prisms. It decomposes on heating. It is only slightly soluble in cold, but is moderately soluble in hot water. It is very soluble in methyl alcohol, ethyl alcohol and glacial acetic acid, but is insoluble in ether.

**Preparation:** Distill 22 ml. of water from 100 g. of 78 per cent syrupy arsenic acid and mix with a 10 per cent excess of phenol (compounds react in molecular proportions). Heat together for 3 hours at a temperature of 147-157° C. with mechanical stirring. Filter from the tarry material which forms and stir barium hydroxide into the mixture until the original brown color turns to pink. Filter and extract several times with ether. Add more barium hydroxide to the aqueous solution until a small portion, after being made alkaline and filtered, gives a test for barium. Now make the solution alkaline to litmus with sodium hydroxide and filter. Remove the excess barium with sodium sulfate and again filter. Evaporate to a small volume to obtain a thick red syrup and add dilute sulfuric acid until the color turns yellow. Separate the tarry material, neutralize, and again evaporate. The crystalline solid which forms is a mixture of sodium sulfate and sodium hydroxyphenylarsonate. Recrystallize from dilute alcohol and dry the compound at 100° C. Finely powder and slowly stir into about one-half its weight of sulfuric acid at 0° C. Now add slowly with stirring and at 0° C. an equal quantity of nitric acid mixed with an equal amount of sulfuric acid. Then let the temperature rise slowly to 10° C. and dilute with 5 volumes of water. Allow the mixture to stand 24 hours and recover the crystals which form.<sup>1</sup>

**Detection of cadmium.** Cadmium salts in an acetic acid solution yield a characteristic yellowish-white crystalline precipitate with nitrophenolarsonic acid.<sup>2</sup> The following procedure is used:

**Procedure.** Add acetic acid to the solution to be tested until the acid concentration is 10 per cent and then add 5 drops of a dilute aqueous solution of the reagent. If a precipitate does not appear immediately, warm for a short time on a water-bath. By means of this test 5γ of cadmium can be detected at a dilution of 1:200,000.

A modification of this procedure, carried out as a microtest on a slide, may be used to detect 0.1γ of cadmium at a dilution of 1:10,000.

A concentration of acetic acid above 20-25 per cent hinders the formation of the precipitate. The precipitate also dissolves in mineral acids, but forms in the presence of sodium acetate if the acid concentration does not exceed 20-25 per cent.

Other metals form precipitates with the reagent but only the cadmium compound is insoluble in acetic acid. Zinc does not interfere if the solution is acid. To prevent the formation of the lead salt, dissolve in concentrated acetic acid and evaporate after the addition of sodium acetate. Bismuth interferes due to the precipitation of the basic bismuth salt. If mercuric ions are present, dissolve in nitric acid, evaporate with sodium acetate, centrifuge the precipitate of mercuric acetate and detect cadmium in the filtrate.

1. J. B. Conant, *J. Am. Chem. Soc.* **41**, 435 (1919).

2. F. Pavelka and E. Kolmer, *Mikrochemie*, **8**, 277-80 (1930); *C.A.* **25**, 1758 (1931).

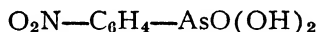
### ***m*-NITROPHENYLARSONIC ACID**

Synonym: *m*-Nitrobenzenearsonic acid

$C_6H_5O_5Na$

Mol. Wt. 247.03

Beil. Ref. XVI, 869.



**Use:** Detection of tin and zirconium.

*m*-Nitrophenylarsonic acid crystallizes as leaves from water. It decomposes on heating without melting. Two parts of the acid dissolve in 100 parts of water. The reagent is slightly soluble in chloroform and benzene, but is insoluble in ether.

**Preparation:** Dissolve 13.8 g. of *m*-nitroaniline in 250 ml. of absolute alcohol and add 10 g. of sulfuric acid and 28 g. of arsenious chloride. Cool the mixture to 0° and diazotize with a saturated aqueous solution containing the calculated amount of sodium nitrite. Add the nitrite to an end-point with starch-iodide paper. At this point, and not before, add 1 g. of cuprous bromide. Stir the mixture thoroughly, and warm at 60° C. until no more nitrogen is evolved. Distill with steam, and crystallize the separated arsonic acid from water.<sup>1</sup>

The following method may also be used:

**Preparation:** Place 10 g. of benzenearsonic acid in 100 ml. flask and dissolve in 80 g. of nitric acid. Boil on an asbestos plate until approximately two-thirds of the nitric acid is distilled and pour the contents of the flask into 75 ml. of water. Cool, filter with suction, and wash the precipitate with water. An additional yield may be obtained by concentrating the mother liquor.<sup>2</sup>

**Detection of zirconium.** *m*-Nitrophenylarsonic acid may be used in place of benzenearsonic acid for the precipitation of zirconium. When a dilute aqueous solution of the reagent is added to a slightly acidified solution to be tested, a strong turbidity appears if zirconium is present.

If zirconium is precipitated in the presence of carminic acid or gallocyanine as zirconium arsenate, intensely colored substances are formed which may be used for the detection of small quantities of zirconium. Only 20 $\gamma$  of zirconium can be detected by this procedure when sodium arsenate is employed as the precipitating agent,<sup>3</sup> but the sensitivity is increased to 5 $\gamma$  of zirconium by substituting *m*-nitrophenylarsonic acid for the alkali arsenate. The following procedure has been proposed by Pavelka:<sup>4</sup>

**Procedure.** Add 0.2-0.3 ml. of 1:4 hydrochloric acid to a small quantity of the solution to be tested and dilute to 1 ml. Add a small crystal of gallocyanine and warm on a water-bath until dissolved. Add 0.5 ml. of a dilute aqueous solution of *m*-nitrophenylarsonic acid and allow the mixture to stand for a few minutes on a water-bath. Mix the solution with one-half its volume of alcohol, boil for a short time, and filter through an Emich filter stick, and then wash with 1 ml. of hot alcohol and dry. By comparing with a blank, zirconium can be detected at a concentration of 1:1,000,000.

Aluminum, cerium and beryllium, do not interfere with this test. Zirconium may be detected in the presence of thorium if the solution is made strongly acid. Titanium must be absent, since it yields a bluish precipitate. Nitrates also must be absent.

**Detection of tin.** *m*-Nitrophenylarsonic acid is a sensitive precipitant for stannic tin, and is useful for detecting the presence of this metal in alloys.<sup>5</sup> By the evaporation of an alloy containing tin with nitric acid, the tin is converted into insoluble hydrated stannic oxide. This is dissolved in dilute hydrochloric acid, and the solution treated with a little *m*-nitrophenylarsonic acid to form a precipitate.

1. G. O. Doak, *J. Am. Chem. Soc.* **62**, 167 (1940).
2. A. Michaelis and H. Loesner, *Ber.* **27**, 265 (1894).
3. L. Moser and R. Lessnigg, *Monatsh.* **45**, 323 (1924).
4. F. Pavelka, *Mikrochemie.* **8**, 345-51 (1930); *C.A.* **25**, 892 (1931).
5. B. Tougarinoff, *Bull. soc. chim. Belg.* **45**, 542-4 (1936); *C.A.* **31**, 63 (1937).

## PROPYLARSONIC ACID



Mol. Wt. 168.01

Beil. Ref. IV, 615.



**Use:** Determination of zirconium.

Propylarsonic acid is obtained as needle-like crystals from alcohol. These melt at 125° C. The compound is readily soluble in water and alcohol, but is insoluble in ether.

**Preparation:** Mix 275 g. of arsenious oxide and 460 g. of potassium hydroxide and add sufficient water for complete solution. Cool, add alcohol until potassium arsenite just begins to precipitate, and then add 460 g. of *n*-propyl iodide. Shake. Add water or alcohol, or both, to prevent precipitation. Place the mixture in a tightly stoppered bottle for several days. At the end of this

period, distill off the alcohol and the ethylpropyl ether which forms. Next add just enough hydrochloric acid to cause precipitation, and pass a stream of chlorine through the mixture until the white precipitate which forms is dissolved and all the iodine is precipitated. Filter, and add magnesia mixture to the cold filtrate until all the arsenate is precipitated. Filter and boil the filtrate from the ammonium magnesium arsenate with more magnesia mixture, and finally precipitate the magnesium salt of propylarsonic acid as pearly white, soapy crystals. To the magnesium salt add the calculated quantity of concentrated sulfuric acid in the cold, and extract with alcohol. Crystals of free propylarsonic acid are obtained by evaporating the alcohol.<sup>1</sup>

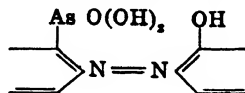
**Determination of zirconium.** When a 5 per cent solution of propylarsonic acid is added to a boiling solution of zirconium chloride in 1.2 N hydrochloric acid, a white precipitate is obtained which yields  $ZrO_2$  upon ignition.<sup>2</sup> This reaction may be used for determining zirconium in the presence of tin, thorium, titanium, manganese, nickel, iron, aluminum, cerium, vanadium, chromium, copper, magnesium, zinc, uranium, molybdenum, cobalt, beryllium, and cadmium. Antimony and bismuth, however, interfere. A little sulfuric acid apparently does no harm. According to Chandlee,<sup>3</sup> the directions of Arnold and Chandlee<sup>2</sup> are inadequate for the separation of zirconium and tin. Geist and Chandlee<sup>4</sup> have used propylarsonic acid for the determination of quantities of zirconium as low as 0.1 per cent in steels containing titanium, aluminum, chromium, cobalt, nickel, copper, uranium, vanadium, thorium, molybdenum and tungsten. They report their results as excellent.

1. W. M. Dehn and S. J. McGrath, *J. Am. Chem. Soc.* **28**, 352 (1906).
2. F. W. Arnold, Jr., and G. C. Chandlee, *J. Am. Chem. Soc.* **57**, 8 (1935); *C.A.* **29**, 2887 (1935).
3. G. C. Chandlee, *J. Am. Chem. Soc.* **57**, 591 (1935); *C.A.* **29**, 2888 (1935).
4. H. H. Geist and G. C. Chandlee, *Ind. Eng. Chem., Anal. Ed.* **9**, 169-70 (1937); *C.A.* **31**, 3817 (1937).

## ***o*-ARSONIC ACIDS OF *o*-HYDROXYAZO COMPOUNDS**

**Use:** Detection and determination of columbium, hafnium, tantalum, thorium, titanium, uranium and zirconium.

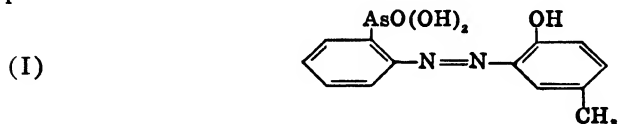
Kuznetsov<sup>1</sup> has shown that *o*-hydroxyazo compounds having an arsono group in the ortho position to the azo group, thus having the grouping,



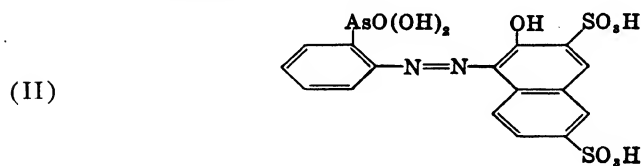
react in an acid medium with many elements to yield precipitates with a simultaneous change of color. The only ions which react in an acid medium to form colored products are thorium, zirconium, hafnium, columbium, tantalum, titanium and uranium. By suitably adjusting the acidity of the solution and using complex-forming reagents, it is possible to increase the specificity of the reaction of the various reagents with the group of elements mentioned above.



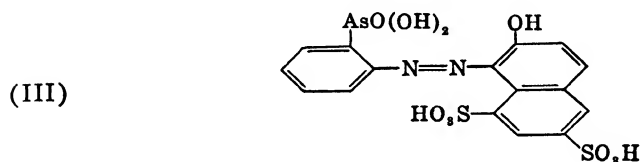
Kuznetsov <sup>1,2</sup> has studied the analytical properties of the following compounds:



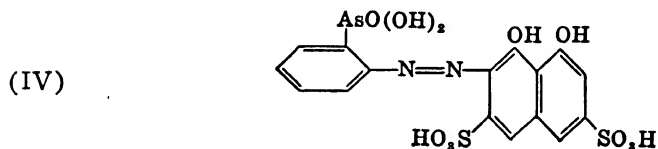
2-(*o*-arsonophenylazo)-*p*-cresol



1-(*o*-arsonophenylazo)-2-naphthol-3,6-disulfonic acid



1-(*o*-arsonophenylazo)-2-naphthol-6,8-disulfonic acid



3-(*o*-arsonophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulfonic acid.

These compounds are prepared by diazotizing *o*-aminophenylarsonic acid and coupling with suitable phenolic compounds. The analytical reactions of these reagents are summarized in Table 10.

TABLE 10.—COLOR REACTIONS OF *o*-ARSONIC ACIDS OF *o*-HYDROXYAZO COMPOUNDS

Rare Earths		
Reagent	Neutral or Slightly Acid Solution	In Hydrochloric Acid Solution
I .....	Yellow	Yellow
II .....	Pink-orange	Orange-yellow
III .....	Orange-yellow	Yellow
IV .....	Blue-crimson	Orange-red

TABLE X.—*Continued*

Titanium (ic)		
I .....	Yellow	Yellow
II .....	Orange	Orange
III .....	Orange-yellow	Orange-yellow
IV .....	Violet	Violet
Zirconium		
I .....	Yellow	Yellow
II .....	Orange	Orange
III .....	Orange-yellow	Orange-yellow
IV .....	Violet	Violet
Tin (ic)		
I .....	Yellow	Yellow
II .....	Orange-yellow	Orange-yellow
III .....	Yellow	Yellow
IV .....	Orange-red	Orange-red
Thorium		
I .....	Brown	Yellow
II .....	Crimson-pink	Crimson-pink
III .....	Pink	Pink
IV .....	Blue-violet	Blue-violet
Columbium		
I .....	Yellow	Yellow
II .....	Yellow	Pink-orange
III .....	Yellow	Orange
IV .....	Yellow	Violet
Tantalum		
I .....	Yellow	Yellow
II .....	Yellow	Pink-orange
III .....	Yellow	Orange
IV .....	Yellow	Red-violet
Uranium		
I .....	Orange	Yellow
II .....	Pink-orange	Orange-yellow
III .....	Brown-yellow	Yellow
IV .....	Blue	Orange-red

The sensitivity of the color reactions with the reagents described above is very great. The color change with thorium and uranium, for example, may be observed at a dilution of 1:1,000,000 or greater. These reactions may be applied both for the detection and for the colorimetric determination of small quantities of the metals listed above.<sup>1</sup>

1. V. I. Kuznetsov, *Compt. rend. acad. sci. (U.R.S.S.)*. **31**, 898-900 (1941) ; *C.A.* **37**, 845 (1943).
2. V. I. Kuznetsov, *J. Gen. Chem. (U.S.S.R.)*. **14**, 914-19 (1944) ; *C.A.* **39**, 4561 (1945).

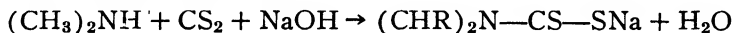
## CHAPTER III

### THE DITHIOCARBAMATES

Carbon disulfide reacts with ammonia, or with primary and secondary amines, to form salts of dithiocarbamic or substituted dithiocarbamic acids.



In the presence of sodium hydroxide, one mole of the amine is freed for conversion into a dithiocarbamate:



A number of dithiocarbamates have been prepared,<sup>1-4</sup> and several of these have been used in analytical procedures.

1. A. Cahours, *Ann. Chim.* [3] **38**, 88 (1853).
2. A. Cahours, *Ber.* **17**, 514 (1884).
3. S. M. Losanitsch, *Ber.* **40**, 2974 (1907).
4. J. V. Dubsky and E. Nejezova, *Chem. Obzor.* **15**, 81-3 (1940).

### AMMONIUM DITHIOCARBAMATE

Synonym: Ammonium sulfocarbamate



Mol. Wt. 110.18

Beil. Ref. III, 216.



**Use:** Detection of aluminum, antimony, bismuth, cobalt, copper, iron, lead, manganese, nickel, silver, tin and zinc.

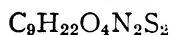
Ammonium dithiocarbamate is a yellow crystalline solid. It is soluble in water, but upon standing in air decomposes to form a product that is no longer completely soluble. The reagent should be stored in a tightly closed bottle.

**Reactions with the metals.** A solution prepared by adding 3-4 volumes of concentrated ammonium hydroxide to carbon disulfide, warming slightly and decanting from the unchanged carbon disulfide,<sup>1,2</sup> may be used as a sensitive reagent for the salts of a number of common metals.<sup>2-6</sup> These reactions are shown in Table 11.

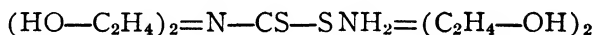
1. E. Mulder, *J. prakt. Chem.* [1] **103**, 178; *Ann.* **168**, 232 (1873).
2. W. Parri, *Giorn. farm. chim.* **73**, 177-82 (1924); *C.A.* **18**, 3569 (1924).
3. G. Gutzeit, *Helv. Chim. Acta.* **12**, 713 (1929).
4. K. Heller and F. Machek, *Mikrochemie.* **19**, 147-61 (1936).
5. J. V. Dubsky and J. Trtilek, *Chem. Obzor.* **9**, 68-9 (1934).
6. N. W. Matthews, *Chemist-Analyst.* **18**, No. 1, 22 (1929).

TABLE 11.—REACTIONS OF METALS WITH AMMONIUM DITHIOCARBAMATE

Metal	Reaction
Lead .....	Red precipitate and yellow solution
Copper .....	Brown precipitate and violet solution
Bismuth .....	Orange-yellow precipitate
Nickel .....	Carmine-red precipitate and red solution
Tin .....	Orange precipitate
Antimony .....	Yellow or orange precipitate in acetic acid
Silver .....	Black precipitate and red solution
Cobalt .....	Green precipitate and green solution
Manganese .....	Brown precipitate
Aluminum .....	White precipitate
Zinc .....	White precipitate
Iron .....	Red brown precipitate, soluble in strong acid

**N,N-BIS (HYDROXYETHYL) CARBAMATE**

Mol. Wt. 181.26

**Use:** Detection of copper.

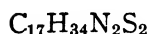
**Detection of copper.** N,N-Bis (hydroxyethyl) carbamate of diethanolamine reacts with solutions of copper salts to form a yellowish-brown compound which may be used for the detection of small quantities of copper.

**Reagent.** Dissolve 10 g. of diethanolamine in 85 ml. of methyl alcohol and add 1 g. of carbon disulfide. Shake well and dilute with methyl alcohol to 100 ml.

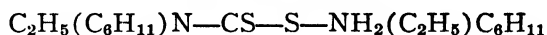
When this reagent is added to a solution containing not more than 0.1 mg. of copper, a compound is formed corresponding in composition to  $C_{10}H_{20}N_2O_4S_4Cu$ . It is soluble in methyl alcohol, ethyl alcohol, acetone, and dioxane but it is insoluble in ether, benzene and carbon tetrachloride.

Cobalt and nickel interfere, but this interference may be eliminated by the addition of sodium cyanide. The copper cyanide complex decomposes in solutions of pH less than 4. Copper then reacts, while nickel and cobalt do not. The pH is adjusted by the addition of a hydrochloric acid-sodium citrate mixture.

1. E. Geiger and H. G. Muller, *Helv. Chim. Acta*, **26**, 996-1003 (1943); *C.A.* **37**, 5331 (1943).

**CYCLOHEXYLETHYLAMINEDITHIOCARBAMATE**

Mol. Wt. 330.56



**Use:** Detection of antimony, bismuth, cobalt, copper, iron, manganese and nickel.

### Determination of copper and iron.

Cyclohexylethylaminedithiocarbamate is a yellow crystalline solid. It has an amine odor, and melts at 93° C. The compound is slightly soluble in cold water, but is more soluble in hot water.

**Detection of metals.** Cyclohexylethylaminedithiocarbamate yields difficultly soluble salts with most common cations, and these precipitates frequently have characteristic colors which make the reaction useful for the identification of such metals as copper, iron, bismuth, manganese, nickel, cobalt and antimony. White compounds are obtained with lead, mercuric, arsenic, antimonous, stannous and zinc salts. Cadmium and pentavalent antimony yield yellowish compounds, as do silver, bismuth and stannous tin from acid solutions, and stannic tin and molybdates from neutral solutions. Copper, manganese, ferrous and ferric salts yield brown precipitates; nickel and cobalt green precipitates; and mercurous salts as gray-black product. Molybdate in the presence of zinc or bismuth salts yields a red-brown compound, while molybdates in acid solution and in the presence of aluminum yield a red compound. Uranyl compounds yield a brick-red product.

These color and precipitation reactions may be used for the detection of many ions. The test is carried out by adding 3 drops of a 0.5 per cent solution of the reagent to 3 ml. of the solution to be tested.<sup>1,2</sup>

**Determination of copper.** The slight solubility of the copper salt of cyclohexylethylaminedithiocarbamate makes possible the quantitative separation of copper from solutions containing no other cations which are precipitated with the reagent. The precipitate cannot be weighed directly, but must be converted to the oxide.<sup>1</sup>

**Procedure.** To a solution containing a few decigrams of copper sulfate in 50-100 ml. of water, add dropwise an 0.8 per cent solution of the reagent (prepared at 80° C.) until precipitation is complete. Then add an excess of 10-50 per cent. Collect the precipitate on paper, wash with an 0.08 per cent solution of the reagent, and dry. Heat until all organic matter is removed, and then ignite to constant weight.

From 0.08 to 2.0 g. of CuO can be determined by this method with an error of 0.5 per cent.

When a solution of cyclohexylethylaminedithiocarbamate is titrated with a solution of copper sulfate, a brown precipitate forms which coagulates and settles almost immediately and leaves a clear supernatant liquid. This behavior has been used as the basis for a titrimetric method for the determination of copper. The end-point of the titration occurs when a precipitate is no longer formed upon the addition of the copper solution.

**Determination of iron.** Iron can be determined by a procedure similar to that described for copper.<sup>1</sup>

**Procedure.** To 10 ml. of a solution containing about 0.1 g. of Fe<sub>2</sub>O<sub>3</sub>, add 10 ml. of 10 per cent ammonium chloride solution and dilute to 100 ml. Add

dropwise 140-190 ml. of 0.8 per cent reagent solution, which corresponds to an excess of 10-50 per cent. Collect the precipitate on paper and wash with 400 ml. of 0.08 per cent reagent solution. Dry carefully at 70° C., and then ignite until all organic matter is removed. Add a few drops of nitric acid, evaporate, and again ignite to  $\text{Fe}_2\text{O}_3$ .

This method is accurate to about 0.6 per cent.

**Separation of iron and chromium.** Since chromium is not precipitated with cyclohexylethylaminedithiocarbamate from a neutral solution, this reagent may be used for the separation of iron and chromium. Further, the chromium compound is very soluble in 0.1 N hydrochloric or sulfuric acid, while the iron compound is practically insoluble.

**Procedure.** To 100 ml. of a solution having an acidity ranging from 0 to 0.1 N in hydrochloric acid, and containing about 0.09 g. of  $\text{Fe}_2\text{O}_3$ , 0.08 g. of  $\text{Cr}_2\text{O}_3$ , and 1 g. of ammonium chloride, add dropwise with shaking an 0.8 per cent reagent solution until precipitation is complete, and then add a slight excess. Filter, wash, and dry as described above. After washing with the dilute reagent, wash with water until the precipitate is free of chloride.

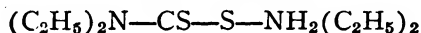
1. M. Herrmann-Gurfinkel, *Bull. soc. chim. Belg.* **48**, 94-103 (1939); *C.A.* **33**, 6746 (1939).
2. J. V. Dubskey and E. Nejezova, *Chem. Obzor.* **15**, 81-3 (1940); *C.A.* **36**, 6948 (1942).

## DIETHYLAMMONIUMDIETHYLDITHIOCARBAMATE

$\text{C}_9\text{H}_{22}\text{N}_2\text{S}_2$

Mol. Wt. 222.49

Beil. Ref. IV, 121.



**Use:** Determination of copper and arsenic.

**Determination of copper and arsenic.** Strafford and co-workers<sup>1</sup> have used diethylammoniumdiethyldithiocarbamate for the extraction of copper and arsenic, and the colorimetric determination of the former, in a scheme for the photometric determination of various metals in organic and medicinal products. The reagent is prepared as follows:

**Preparation:** *Stock solution:* Dilute 3.0 ml. of redistilled diethylamine to 10 ml. with chloroform, and add slowly with stirring 1.0 ml. of redistilled carbon disulfide, previously diluted to 10.0 ml. with chloroform. Cool and store in a dark-colored, glass-stoppered bottle.<sup>1</sup>

*Extraction reagent:* Dilute 5.0 ml. of the stock solution to 100 ml. with chloroform. Prepare the stock solution each week, and dilute daily.

**Determination.** Because of the very small quantities of the metals which are determined, special precautions must be taken to ensure purity of reagents and cleanliness of the apparatus, but in general the determination of copper and arsenic is based on the following steps: Decompose a 2-g. sample in a 100-ml. Kjeldahl flask with sulfuric, nitric, and perchloric acids. Dilute the

solution and add sufficient hydrochloric acid to give a minimum acid concentration of 2 N. Then reduce the arsenic by adding 2.0 ml. of 20 per cent sodium or potassium iodide solution, warming to 40° C., and adding 0.5 ml. of 5 per cent sodium metabisulfite solution. Dilute the solution to 35 ml. and extract the arsenic and copper, using 5- and then 2-ml. portions of the extraction reagent. Determine copper in the extract in the usual manner as the carbamate, using the characteristically-colored copper complex for the colorimetric estimation. Then determine arsenic in the extract after decomposing with sulfuric acid, perchloric acid, and molybdate by means of the molybdenum blue reaction.<sup>2</sup>

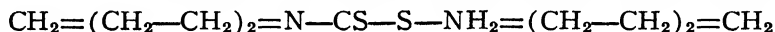
This reagent is said to be superior to sodium diethyldithiocarbamate for the extraction of arsenic.

1. M. Grodski, *Ber.* **14**, 2756 (1881).

2. N. Strafford, P. F. Wyatt and F. G. Kershaw, *Analyst.* **70**, 232-46 (1945); *C.A.* **39**, 4297 (1945).

## PIPERIDINIUM PIPERIDYLDITHIOFORMATE

Synonym: Pentamethylenedithiocarbamic acid, piperidine salt



**Use:** Determination of copper.

**Preparation:** Pentamethylene dithiocarbamic acid is formed by mixing alcoholic solutions of molecular quantities of piperidine and carbon disulfide with an excess of aqueous ammonia. Separate the crystals which form with suction, and wash with alcohol and ether. This compound forms a salt in alcoholic solution with piperidine.<sup>1-4</sup>

**Determination of copper.** Piperidinium piperidyldithioformate reacts with a neutral solution of a cupric salt to form a yellow-brown color which can be used satisfactorily for the colorimetric determination of 0.002-0.1 mg. of copper. The copper solution must contain no iron. The color is very stable and is not affected by the presence of a slight excess of acid or alkali. Cadmium, mercury and bismuth do not interfere:<sup>4-6</sup>

The following method is used for the determination of copper in organic matter:

**Procedure.** Place a weighed sample of the material in a silica dish and heat on a hot plate until charred. Place in a muffle furnace and heat for 30 minutes at not above 400° C. When cool, add a few ml. of fuming nitric acid and evaporate to dryness on a hot plate. Again heat in the furnace if large quantities of nitric acid remain, or treat with fuming nitric acid if only a small amount is unchanged. Repeat if necessary.

Dissolve the ash in 10 ml. of 1:1 hydrochloric acid and dilute to 100 ml. Add 2 drops of concentrated nitric acid and heat to boiling. Pass a stream of hydrogen sulfide through the mixture until cold. Allow the precipitate to settle, filter through a sintered glass crucible using suction, and then wash with water which has been acidified with acetic acid and saturated with hydrogen sulfide



until iron is no longer detected in the filtrate. Place the crucible on a silica triangle over a small crystallizing dish which is in turn placed on a water-bath, and add fuming nitric acid to the crucible. When no more liquid remains in the crucible, wash with water and allow to remain on the water-bath until the copper solution has evaporated. Transfer the crystallizing dish to a hot plate and heat until acid fumes are no longer given off, but be careful not to decompose the nitrate. Dissolve the residue in water and transfer to a graduated glass-stoppered flask. To a suitable aliquot of the neutral solution, add 1 ml. of a 0.1 per cent alcoholic solution of the reagent and allow to stand until the maximum color develops. Compare with a standard prepared by dissolving 0.393 g. of pure copper sulfate in a liter of solution. One ml. of this solution contains 0.1 mg. of copper.

This method is more accurate for quantities of 0.01-0.08 mg.

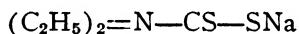
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2. A. Cahours, *Ann. Chim. et Phys.* [3] **38**, 88.
3. S. M. Losanitsch, *Ber.* **40**, 2974 (1907).
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## SODIUM DIETHYLDITHIOCARBAMATE

$C_5H_{10}NS_2Na$

Mol. Wt. 171.25

Beil. Ref. IV, 121.



**Use:** Detection of cadmium, cobalt, copper, lead, manganese, mercury, nickel, strontium and zinc.

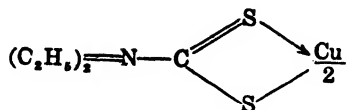
Determination of cobalt, copper, indium, palladium, platinum and zinc.

Sodium diethyldithiocarbamate is a white crystalline compound. It is readily soluble in water, but is less soluble in alcohol.

**Preparation:** Prepare a 20 per cent aqueous solution of diethylamine containing 1 mole of the amine and cool to below 10° C. Stir well, while keeping below 10° C., and add slowly 1.05 moles of carbon disulfide. Then add slowly 1 mole of sodium hydroxide in a 10 per cent aqueous solution. Allow to warm to room temperature. A suitable reagent is prepared by diluting this solution with water to the desired concentration.<sup>1</sup>

**Detection of copper.** In 1908 Delepine<sup>2</sup> published a paper describing the properties of methylthiocarbamates, including the copper compounds, and in the same year<sup>3</sup> he published a paper on the detection of copper and iron with a solution of dialkyl dithiocarbamate.

Sodium diethyldithiocarbamate reacts with solutions of copper salts to give a brownish-yellow color or precipitate. This color is the same in neutral, alkaline or acid solutions. The compound formed in this reaction has been assigned the following formula:<sup>4</sup>



The formation of this compound has been used for the detection and determination of copper.

Callan and Henderson <sup>6</sup> have studied the reactions of sodium diethyldithiocarbamate with various metals, and their results are tabulated in Table 12:

TABLE 12.—REACTION OF SODIUM DIETHYLDITHIOCARBAMATE WITH METALLIC SALTS

Metal	Reagent Is a 20 Per Cent Solution Added to a 5-10 Per Cent Solution of the Metal Salt	Reagent Is a 0.1 Per Cent Solution Added to Solution Containing 1-20 p.p.m. Metal
Aluminum ....	White curdy precipitate	White opalescence
Antimony .....	Yellow-white precipitate	White turbidity
Barium .....	Slight white precipitate	Clear
Bismuth .....	White curdy precipitate	White turbidity
Cadmium .....	Creamy white precipitate	White turbidity
Calcium .....	Slight white precipitate	Clear
Chromium ....	Dark green precipitate	Very faint turbidity
Cobalt .....	Greenish-brown precipitate	Yellow coloration
Iron (ous) ....	Light brown precipitate	Brown color
Iron (ic) .....	Very dark brown precipitate	Deep brown color
Lead .....	White curdy precipitate	White turbidity
Magnesium ...	Slight white precipitate	Clear
Manganese ....	Dirty yellow precipitate	Very faint turbidity
Mercury (ous) ..	White precipitate	Very faint turbidity
Mercury (ic) ..	Yellow white precipitate	White turbidity
Nickel .....	Yellow-green precipitate	Yellow-white turbidity
Silver .....	Pale yellow precipitate	Very faint turbidity
Tin (ous) ....	Buff precipitate	White turbidity
Tin (ic) .....	Pale buff precipitate	.....
Titanium .....	Dirty yellow precipitate	Yellow-white turbidity
Uranium .....	Bright orange precipitate	Golden-yellow color
Zinc .....	White curdy precipitate	White turbidity

In the absence of interfering substances, Laget <sup>6</sup> recommends the following procedure:

**Procedure.** To 5 ml. of the solution to be tested, add 5 ml. of 95 per cent alcohol and 1 ml. of a 1 per cent alcoholic solution of sodium diethyldithiocarbamate. The brownish-yellow color appears with as little as 0.01γ of sodium diethyldithiocarbamate.

If zinc is present in addition to copper, perform the test by mixing 10 ml. of amyl alcohol ( $d = 0.880$ ) and 15 ml. of 95 per cent alcohol, and to the mixture add 5 ml. of the solution to be tested and 1 ml. of a 1 per cent alcoholic solution of sodium diethyldithiocarbamate.

To eliminate interference due to cadmium, mix 12 ml. of amyl alcohol and 15 ml. of 95 per cent alcohol and then add 5 ml. of the solution to be tested and 1 ml. of 1 per cent alcoholic solution of reagent.

Clarke and Hermance<sup>7</sup> have studied the sensitivity of the dithiocarbamate reaction and report that with a drop method employing sodium diethyldithiocarbamate, 0.2γ of copper can be detected. With paper impregnated with zinc diethyldithiocarbamate, and using a special technique, as little as 0.002γ of copper can be detected. Yagoda<sup>8</sup> has carried out the copper reaction semi-quantitatively by applying the spot test to reaction fields of unit surface area, and carrying out the test so that the colored reaction products are uniformly distributed over the entire surface. In this way it is possible to make a colorimetric estimation of the copper per cent. The reagent is zinc diethyldithiocarbamate.

61-50

**Determination of copper.** A brown precipitate of the very slightly soluble copper carbamate is formed when an aqueous solution of sodium diethyldithiocarbamate is added to a neutral, slightly acid, or ammoniacal solution of a cupric salt. In very dilute copper solutions, a colloidal suspension is formed which is suitable for a colorimetric comparison.<sup>5,9,63</sup> Gum tragacanth, gelatin,<sup>10</sup> and gum arabic<sup>19</sup> may be used as protective colloids to prevent coagulation of the colloidal precipitate.

The copper carbamate is soluble in a number of organic liquids, such as amyl alcohol, amyl acetate, bromobenzene, carbon tetrachloride, and chloroform. A number of colorimetric methods have been based on the extraction of the copper compound with one of these liquids, and the colorimetric comparison of the resulting yellow-brown solution, or the measurement of its light absorption. The extraction method is generally preferred, since in this way difficulties arising from the use of colloidal suspensions are eliminated. Further, by using the extraction method the sensitivity of the reaction is increased, and interference by certain colored ions can more readily be prevented.

MacFarlane<sup>9</sup> used amyl alcohol for the extraction of copper carbamate. Thatcher<sup>11</sup> reports, however, that if isoamyl alcohol (redistilled at 129-131° C.) is used instead of amyl alcohol, a sharp separation of the liquid layers is obtained. This is not true when amyl alcohol is used. Drabkin<sup>65</sup> has recommended isoamyl acetate because of its low volatility and low specific gravity, which makes unnecessary the use of separatory funnels. Williams<sup>12</sup> recommends extracting the yellow color with chloroform. Haddock and Evers<sup>13</sup> recommend extracting the color with chloroform and determining the intensity of the yellow color in a Lovibond tintometer. Conn and co-workers,<sup>14</sup> however, prefer to match the colors obtained in a series of standards in aqueous solution if the original solution is not colored. Solutions of copper diethyldithiocarbamate in carbon tetrachloride or isoamyl acetate are fairly stable, and no appreciable change in color intensity occurs during a period of several hours.

The pH of the solution has but slight effect upon the color intensity of the copper carbamate in the organic solvent in the range 5.7-9.2.<sup>65</sup>

Many of the heavy metals form slightly soluble compounds with sodium diethyldithiocarbamate, and most of these are somewhat soluble in organic liquids.

Zinc, cadmium, mercuric, silver, lead and tin salts yield white carbamates, while all others are highly colored. Ferric iron, for example, yields a brown-black precipitate in neutral or acid solution, but does not react in an ammoniacal citrate solution of pH 9 or greater.<sup>13</sup>

Unless proper precautions are taken, iron interferes with the copper determination, and various procedures have been suggested whereby this interference can be removed. Callan and Henderson<sup>5</sup> have suggested that the iron be removed by precipitation with ammonium hydroxide. Grendel<sup>15,16</sup> has proposed that the copper be separated by electrolytic deposition to remove iron. The copper is then dissolved, treated with sodium diethyldithiocarbamate, extracted with carbon tetrachloride and compared in a colorimeter. Haddock and Evers<sup>18</sup> recommend the determination of copper in the presence of iron without first removing the latter by adding citric acid and ammonium hydroxide to the solution containing copper and ferric iron:

**Procedure.** To a solution containing ferric iron and not more than 0.1 mg. of copper in a volume not greater than 50 ml., add 2 g. of pure citric acid (sufficient for 0.1 g. iron), and then add ammonium hydroxide until the pH is greater than 9.0. Dilute to 70 ml. and add 10 ml. of a 0.1 per cent solution of sodium diethyldithiocarbamate. Extract the mixture with four successive 2.5-ml. portions of chloroform, and repeat the extraction if the fourth shows more than a trace of color. Dilute the carbon tetrachloride extracts to 20 ml. and determine the color in a Lovibond tintometer, using the yellow color only. By the use of an empirical curve, the copper content is obtained. The results obtained by this method agree within 0.003 mg., and quantities of copper as small as 0.005 mg. can be determined in the presence of 0.25 g. of iron. Results are shown in Table 13.

TABLE 13.—DETERMINATION OF COPPER IN THE PRESENCE OF IRON

FeCl <sub>3</sub> ·6H <sub>2</sub> O g.	Cu Present mg.	Cu Added mg.	Total Found mg.
0.5	0.022	0.010	0.031
0.5	0.022	0.020	0.041
0.6	0.055	0.030	0.088
0.6	0.055	0.005	0.059
1.0	0.008	0.010	0.018

Alkali metals, nitrates up to 0.75 mg., sodium phosphate up to 0.25 g. of phosphate, and calcium phosphate up to 0.3 g. do not interfere. The above method also gives satisfactory results in the presence of aluminum and zinc if the quantity of aluminum does not exceed 0.2 g. or the quantity of zinc does not exceed 0.1 g. If iron is absent, aluminum or zinc may be dissolved in an excess of sodium hydroxide.

If no more than a trace of iron is present, copper may be determined in the presence of not more than 0.2 g. of manganese by adding 2 g. of citric acid and 5 ml. of 5 per cent sulfur dioxide solution, followed by an excess

of ammonia. In the absence of iron, traces of copper may be determined in the presence of stannic salts by adding an excess of sodium hydroxide and ammonia as in the determination in the presence of aluminum and zinc.

Haddock and Evers<sup>13</sup> have shown that iron and lead can be removed by the use of ammonium hydroxide, but with zinc the addition of 2-5 ml. of concentrated ammonium hydroxide per 100 ml. of solution prevents interference with the copper reaction, providing zinc does not exceed 0.1 g. per 100 ml. of solution.

MacFarlane,<sup>9</sup> Warburg,<sup>17</sup> and Drabkin and Waggoner<sup>18</sup> have used ammonium pyrophosphate to eliminate interference by iron with the copper-sodium diethyldithiocarbamate reaction, and also have extracted the color with amyl alcohol. The alcohol extraction serves two useful purposes: (1) The copper compound is not very soluble in water and may cause a turbidity; and (2) the copper compound is removed from the colored ferric ions in the aqueous phase.

Hoar<sup>19</sup> recommends two procedures for the determination of copper in the presence of moderate quantities of iron. The first of these is a modification of the method of Haddock and Evers<sup>13</sup> in which citric acid, ammonia and a little gum arabic are added to the copper solution, followed by the addition of the reagent. A correction is made for the slight yellow tint caused by the presence of iron. In the second method the iron is prevented from reacting by the addition of sodium pyrophosphate, but no ammonium hydroxide is added and no correction is made for the color of the ferric iron. Otherwise, the procedure is the same:

**Reagents.** *Sodium diethyldithiocarbamate solution:* This is a 0.2 per cent solution.

*Sodium pyrophosphate solution:* Dissolve 40 g. of sodium pyrophosphate in cold water and dilute to 1 liter.

**Procedure.** Place 10-20 ml. of a nearly neutral solution containing 0.005-0.025 mg. of copper in a 50-ml. flask, and add 10 ml. of the sodium pyrophosphate solution and 5 ml. of a 1 per cent solution of gum arabic. Mix well, add 5 ml. of sodium diethyldithiocarbamate solution and dilute to 50 ml. Measure the yellow units of color in a 1-cm. cell of a Lovibond tintometer and compare with a standard curve. The presence of zinc may cause a turbidity which can be avoided by making the solution strongly ammoniacal.

Hoar<sup>20</sup> has used this method for the determination of copper in mild steel.

Nickel, cobalt, and bismuth interfere most seriously with the copper determination. In ammoniacal citrate solutions these metals yield greenish-yellow, dull green, and yellow precipitates, respectively, and impart similar colors to the organic extractant. The color formed by the copper carbamate is destroyed by cyanide, while that due to bismuth is not. Drabkin<sup>65</sup> has used this fact for the elimination of interference by bismuth in the copper determination. He measured the transmittancies of two sample solutions, one containing cyanide and the other without, and then found copper by difference.

Interference by nickel and cobalt is prevented by adding 1 ml. of 0.5 per cent dimethylglyoxime solution to the sample solution and then adding ammonia.<sup>20</sup>

The nickel precipitate is removed by centrifugation, and cobalt remains in the aqueous solution as an orange complex which is not extracted by carbon tetrachloride. Uranium reacts with sodium diethyldithiocarbamate in a neutral medium to yield a strong yellow color, but not in an ammoniacal citrate solution. Manganese may interfere by causing a pink color in the organic layer, but this color is unstable and virtually disappears after a time if only small quantities of manganese are present. Pyrophosphate also reduces the color due to manganese.<sup>64</sup>

Copper is seldom present in natural water, but the use of copper and brass pipes in water systems, as well as the use of copper sulfate as an algacide, has made necessary the development of a simple and rapid method for the determination of this element in water. The carbamate method appears to be one of the best available for a colorimetric procedure.<sup>21-24,60</sup> Sodium diethyldithiocarbamate is not specific for copper, but interfering substances are not common in water, and it is easy to detect their presence. Both zinc and lead produce a white turbidity, and iron, which also interferes, should be removed by filtration after precipitation with ammonium hydroxide.

**Reagent.** Dissolve 1 g. of sodium diethyldithiocarbamate in a liter of distilled water, and store in a dark glass bottle, which is protected from light.

**Standard copper solution:** Dissolve 0.393 g. of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in 1 liter of distilled water. Dilute 25 ml. of this solution to 250 ml. One ml. of the diluted solution contains 0.01 mg. of copper.

**Procedure.** Place 50 ml. of the sample to be analyzed in a 50-ml. Nessler tube. The quantity of copper should not exceed 0.1 mg., since greater quantities give colors which are too deep for an accurate comparison. In case the sample contains more than 0.1 mg. of copper, use an aliquot portion and dilute to 50 ml. Add 5 ml. of 1:5 ammonium hydroxide solution, and filter if a precipitate forms. Now add 5 ml. of the sodium diethyldithiocarbamate solution and compare within one hour with standards similarly prepared. The standards should be prepared to contain from 0.005-0.05 mg. of copper.

Frequently in making the copper determination a turbidity appears which interferes with the color comparison. Should this occur, extract the color by shaking the reaction mixture with successive 3- to 5-ml. portions of carbon tetrachloride until the extracts appear colorless. If carbon tetrachloride is used to extract the color, the standard solutions used for comparison should be extracted in the same manner and with precisely the same volume of tetrachloride. Transfer the extracts from both sample and standards to a series of Nessler tubes for comparison. Since the extracts of both sample and standards have been made with the same volume of carbon tetrachloride, it is not necessary to dilute the solutions to 50 ml.

Atkins<sup>25</sup> and Galtsoff<sup>26</sup> have used sodium diethyldithiocarbamate for the determination of copper in sea water.

The use of sodium diethyldithiocarbamate has been extensively applied to the determination of copper in biological materials. Various investigators<sup>9,12,14-</sup>

<sup>16,27</sup> have used sodium diethyldithiocarbamate for the determination of copper in milk and dairy products; for the determination of copper in blood and organic material; <sup>9</sup> in plants; <sup>28-32</sup> fabrics; <sup>33</sup> and in dyes, intermediates, rubber and rubber chemicals. <sup>34</sup> Ensslin <sup>35</sup> has used the method of Callan and Henderson for the determination of copper in refined zinc, and Kelly and Malloy <sup>36</sup> have used a similar procedure to test for the completeness of electrodeposition of copper. Thomas and co-workers <sup>37</sup> have used sodium diethyldithiocarbamate for the colorimetric determination of copper in steel containing less than 0.25% nickel, and Haywood <sup>38</sup> has used the same reagent to determine copper in various ferrous materials. Bertoldi <sup>39</sup> applied the carbamate reaction to the colorimetric determination of copper in aluminum alloys.

Ensslin <sup>37</sup> has used the following procedure for determining copper in soft and hard products containing lead and thallium:

**Procedure.** Decompose a 2-10 g. sample with concentrated sulfuric acid and a few drops of fuming nitric acid. Fume the solution, cool, and strongly dilute with water. Filter off lead sulfate, treat a definite volume with 20 per cent citric acid, and make weakly alkaline with ammonia. Now add 10-15 ml. of 0.1 per cent solution of sodium diethyldithiocarbamate and shake with carbon tetrachloride in a separatory funnel. Repeat the extractions with carbon tetrachloride until all the color is removed from the aqueous solution. Filter the brown-colored tetrachloride extracts through a dry filter and dilute to a definite volume, and compare with standards in a colorimeter, comparator, or photometer.

Copper can be determined in thallium metal by this procedure when present only to the extent of 0.002 per cent. For greater sensitivity it has been recommended that the copper be precipitated from a larger volume with hydrogen sulfide in acid solution, and the copper determined as described above.

Karsten <sup>38</sup> has applied the principle of titrimetric colorimetry to the determination of copper with sodium diethyldithiocarbamate. Urech <sup>39</sup> has also used the colorimetric titration for determination of copper in aluminum and aluminum alloys.

**Determination of cobalt and nickel.** Like copper, salts of cobalt and nickel react with sodium diethyldithiocarbamate to give colored compounds.<sup>9</sup> These compounds are soluble in ether, benzene and other organic liquids. Scacciati <sup>40</sup> has used this property of nickel and cobalt salts for separating the latter in the analysis of zinc ores and zinc electrolytes. The method is based upon formation of complexes of cobalt and nickel with sodium diethyldithiocarbamate, even in the presence of excess of ammonium hydroxide, and the extraction of these complexes with chloroform.

**Procedure.** Treat a solution containing as little as 1-30 mg. of nickel and cobalt in the presence of an excess of zinc with 20-30 g. of ammonium chloride and then add ammonium hydroxide dropwise until the precipitate which first forms redissolves. Shake the solution with 0.5-1.0 g. of sodium diethyldithiocarbamate dissolved in water in a separatory funnel. Extract this solution with successive portions of chloroform until the chloroform layer is no longer

colored. Then shake the chloroform extract with two successive portions of ammonium hydroxide to remove traces of zinc salts, and after the separation distill the chloroform. Treat the residue with nitric acid and bromine to redissolve the cobalt and nickel, which are then determined by any of the usual procedures.

Quantities of the metals ranging up to 5 mg. have been determined by this method with an accuracy of 10 per cent, while larger quantities may be determined with an accuracy of 2 per cent or better.

**Determination of zinc.** Atkins<sup>41,42</sup> has used sodium diethyldithiocarbamate for the turbidimetric determination of zinc in sea water. Zinc may be determined in concentrations ranging from 0.05-25 p.p.m. Unlike the precipitate formed with lead, the zinc turbidity disappears on addition of ammonium hydroxide:

**Procedure.** Add 10 ml. of 0.1 per cent sodium diethyldithiocarbamate solution to 100 ml. of water to be analyzed, and to the same volume of standard solutions of zinc sulfate in Nessler tubes. Compare the resulting turbidity. Standards are prepared by diluting a 0.01 N zinc sulfate solution.

Atkins<sup>41,42</sup> claims that this method is as delicate as the ferrocyanide method, but Wenger and co-workers<sup>43</sup> do not recommend it due to the fact that the reagent is unstable.

Sodium diethyldithiocarbamate is used in the analysis of zinc for the purpose of eliminating interference as a preliminary to the final determination with dithizone.<sup>44-46</sup> For a discussion of this use, read section on the determination of zinc in the chapter on dithizone.

**Determination of platinum.** Pollard<sup>47-55</sup> has used sodium diethyldithiocarbamate for the determination of platinum in cupellation beads:

**Procedure.** Concentrate less than 2 mg. of platinum and gold in a bead containing 5 mg. of silver and no copper or other base metal. Clean the bead and flatten, and then heat with 2 drops of 6 N nitric acid, which leaves the gold and a part of the platinum undissolved. Palladium colors the nitric acid yellow. Add 6 ml. of concentrated hydrochloric acid and heat to complete the solution of gold and platinum. Treat with stannous chloride to precipitate the gold and reduce the platinum to the highly colored platinous state. Filter off the precipitated gold. Cool, add 5 ml. of benzene, close the tube and shake well. Then determine the platinum by adding a standard sodium diethyldithiocarbamate solution from a microburet until the hydrochloric acid is colorless. Sodium diethyldithiocarbamate reacts with platinum to form a compound which is soluble in benzene, and therefore the end-point is represented by the disappearance of the color of the platinum compound in the hydrochloric acid solution.

Palladium also reacts with sodium diethyldithiocarbamate to cause serious interference with the platinum determination, but other platinum metals do not interfere. Tellurium and arsenic cause some trouble.



**Determination of palladium.** Pollard<sup>56</sup> has used sodium diethyldithiocarbamate for the determination of palladium by a method similar to that described for platinum. Palladium must be present as the chloride in an approximately 50 per cent hydrochloric acid solution. Stannous chloride reacts with palladium chloride in a hydrochloric acid solution to give a series of color changes which vary with the strength of the acid. A solution of 0.01 mg. of palladium in 10 ml. of 1:1 hydrochloric acid gives only a transient brown tinge with stannous chloride, but upon adding a drop of 0.05 per cent mercuric chloride solution and shaking, a reddish-brown color appears. The colored compound formed with stannous chloride alone is soluble in amyl acetate, while that formed on the subsequent addition of mercuric chloride is not. Both compounds react with sodium diethyldithiocarbamate to form substances which are soluble in benzene. This series of reactions has been used in a micromethod for the analysis of palladium.

**Reagents.** *Sodium diethyldithiocarbamate solution:* Dissolve 0.5 g. of sodium diethyldithiocarbamate in 100 ml. of water and filter from any oily impurities. Adjust the strength of the sodium diethyldithiocarbamate solution by titrating against a standard palladium solution. This reagent should not be kept for more than 1 month.

*Stannous chloride solution:* Heat 400 g. of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  with 200 ml. of concentrated hydrochloric acid for several hours in the presence of granulated tin and filter through asbestos.

*Standard palladium solution:* Dissolve 0.1 g. of palladium metal in 2 ml. of 3:1 aqua regia.

**Procedure.** To a palladium solution containing 0.01-1.0 mg. of palladium add 5 ml. of hydrochloric acid (sp. gr. = 1.16), 5 ml. of water and 1 ml. of stannous chloride solution. Allow the mixture to stand until the color has developed and then add 5 ml. of benzene. Titrate the mixture from a microburet with the sodium diethyldithiocarbamate solution previously standardized against a 0.1 per cent palladium solution. After each addition of the reagent, close the test tube with a rubber stopper, shake, and allow the benzene to separate. Continue the titration until the aqueous layer is nearly colorless and then add 5 drops of a 0.01 per cent mercuric chloride solution. Shake until the red-brown color develops, and then continue the titration until all the color has disappeared.

For solutions containing 0.001-0.01 mg. of palladium, use 1 ml. of concentrated hydrochloric acid, 1 ml. of water, 2 drops of stannous chloride solution and 1 drop of mercuric chloride solution, and titrate with the sodium diethyldithiocarbamate solution that has been diluted to one-tenth its original concentration.

**Determination of indium.** Sodium diethyldithiocarbamate reacts with indium in a neutral or weakly acid solution to form a voluminous white precipitate corresponding in composition to  $\text{In}[\text{SCS}-\text{N}(\text{C}_2\text{H}_5)_2]_3$ .

Ensslin<sup>57</sup> has used this reaction for the determination of indium. The solution to be analyzed must not contain more than 100 mg. of indium, since with

greater quantities a large volume of a poorly filterable precipitate is formed. Allow the mixture to stand for eight hours after adding the reagent, and filter through a glass filtering crucible. Wash the residue with water and dry at 105° C. and weigh. Lead, cadmium, zinc, copper and iron interfere with this determination.

**Detection of manganese, cadmium, mercury, lead and cobalt.** Grant and Meggy<sup>58</sup> have investigated the crystal forms of a number of metallic salts of sodium diethyldithiocarbamate with a view of using this reaction for the micro-chemical detection of the cations.

**Reagent.** Shake a little solid sodium diethyldithiocarbamate with water in a test tube and filter. Use the clear filtrate.

**Procedure.** Place 0.3 ml. of the reagent in a test tube (60 mm. × 6 mm.) fitted with a solid ground glass stopper and add 0.3 ml. of the neutral solution to be tested and 0.2 ml. of benzene. Shake well and carefully transfer the benzene layer to a microscope slide. Be careful that no water is transferred with benzene solution. Allow the benzene to evaporate at room temperature and then examine the residue under a low-power microscope. The following results have been obtained:

(a) Cadmium: Large isolated hexagonal crystals. Sensitivity 0.01 mg. Cd (1:20,000).

(b) Mercuric: Brown plates. Sensitivity 0.1 mg. Hg (1:2,000).

(c) Manganese: Elongated hexagonal crystals. Sensitivity 0.01 mg. Mn (1:20,000). Ferric iron and copper interfere with this test.

(d) Lead, zinc and strontium: Elongated rectangular plates. Sensitivity of the lead is about the same as that of mercury.

(e) Cobalt: Rectangular long brownish-green plates. The principle value of this reaction lies in the fact that the nickel complex is entirely different and makes possible the detection of cobalt in the presence of nickel.

Wenger and co-workers,<sup>59</sup> who have studied the various methods for detecting manganese, do not recommend the use of sodium diethyldithiocarbamate for this purpose. The reaction with manganese resembles that of other members of the same analytical group such as zinc and iron. The reaction is positive but appears to be of less interest than others which have been proposed.

**Determination of lead.** Thompson and Anderson<sup>60-62</sup> eliminated interference by iron in the lead determination with dithizone by a preliminary extraction with sodium diethyldithiocarbamate. For the details of this procedure, see section on dithizone.

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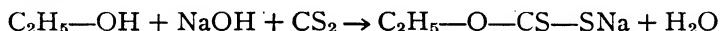
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## CHAPTER IV

### THE XANTHATES

The alcohols react with carbon disulfide in the presence of an alkali to form compounds called xanthates or xanthogenates. This reaction is illustrated by the following equation



in which sodium hydroxide and ethyl alcohol form sodium ethyl xanthate. A number of these compounds give useful color reactions with various metals, especially copper, and have proved useful in inorganic analysis. The formation of yellow copper salts is characteristic for the xanthates, and depends on the group  $\text{—O—CS—SH}$ . Various radicals may be bound to this group without influencing the character of the color reaction, although the sensitivity of the test may be affected. Tamchyna<sup>1</sup> has studied the reactions of a number of xanthates with copper, and his results are shown in Table 14. The tests were carried out by adding 0.5 ml. of the xanthate solution and 0.5 ml. of 1N hydrochloric acid to 5 ml. of the copper solution. One-ml. portions of the cetyl and myricyl reagents were used.

TABLE 14.—REACTIONS OF XANTHATES WITH COPPER

Xanthate	Formula	Concentration Limit	Limit of Identification $\gamma$ per ml.
Potassium ethyl xanthate	$\text{C}_2\text{H}_5\text{—O—CSSK}$	1:2,500,000	3.75
Potassium butyl xanthate	$\text{C}_4\text{H}_9\text{—O—CSSK}$	.....	....
Potassium cetyl xanthate	$\text{C}_{18}\text{H}_{35}\text{—O—CSSK}$	1:5,000,000	1
Potassium isoamyl xanthate	$(\text{CH}_3)_2\text{C—CH}_2\text{—O—CSSK}$	1:3,300,000	1.5
Potassium myricyl xanthate	$\text{C}_{30}\text{H}_{61}\text{—O—CSSK}$	1:5,000,000	1

The reagents were prepared in the same manner as that described for potassium ethyl xanthate (page 97), by substituting the higher alcohols for ethyl alcohol. The cetyl and myricyl compounds were used in cold saturated alcoholic solutions, while the others were used in 0.5 per cent aqueous solution.

TABLE 15.—REACTIONS OF XANTHATES WITH MOLYBDENUM

Xanthate	Concentration Limit	Limit of Identification
Potassium isobutyl xanthate .....	1:1,500,000	0.07 $\gamma$ in 0.1 ml.
Potassium isoamyl xanthate .....	1:2,000,000	0.05 $\gamma$ in 0.1 ml.
Potassium cetyl xanthate .....	1:500,000	0.06 $\gamma$ in 0.03 ml. (spot test)

The xanthates also react with molybdenum in a weakly acid solution to give a red-violet color. Tamchyna<sup>1</sup> reports the results of test with various xanthates in Table 15.

The reagents were used in 0.5 per cent aqueous solution.

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## CELLULOSE XANTHATE

Synonym: Viscose

**Use:** Detection of bismuth, cobalt, copper and lead.

Cellulose xanthate reacts with solutions of various metallic salts to give characteristic colors. The most useful analytical reactions are with lead, bismuth, copper and cobalt. Technical viscose may be used as the reagent, and a 0.05 per cent aqueous solution is suitable. The test may be carried out either in a neutral or weakly acid solution. After applying the test, the weak yellow color of the viscose solution is removed by acidifying with a few drops of 1 N hydrochloric acid. The colors formed in the reactions and their sensitivities are given in Table 16.

TABLE 16.—REACTIONS OF METALS WITH VISCOSE

Metal	Color	Sensitivity	
		1 ml. Test	Spot Plate (0.05 ml.)
Lead .....	Red color	1:200,000	0.001 mg.
Bismuth .....	Brown-red color	1:200,000	0.0005 mg.
Copper .....	Brown precipitate	1:400,000	0.00025 mg.
Cobalt .....	Green-brown color	1:170,000	0.001 mg.

Lead sulfate also reacts with the viscose reagent to give a red color. This makes possible the detection of lead in the presence of bismuth: lead is precipitated as the sulfate from the bismuth solution, and the test is applied to the precipitate. Copper as the complex cyanide does not react.

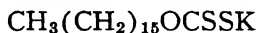
1. J. Tamchyna, *Chem. Listy*, 24, 31 (1930).
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## POTASSIUM CETYLXANTHATE



Mol. Wt. 356.65

Beil. Ref. III, 212.



**Use:** Detection of molybdenum.

This compound is obtained as greasy crystals by crystallizing from alcohol. It is difficultly soluble in cold alcohol.

**Detection of molybdenum.** Potassium cetyl xanthate has been proposed by Tamchyna <sup>1,2</sup> as a sensitive reagent for molybdenum.

**Reagents.** *Potassium cetyl xanthate solutions:* Saturate 10 ml. of cetyl alcohol with potassium hydroxide and add an excess of carbon disulfide.

*Potassium cetyl xanthate test paper:* Impregnate a strip of filter paper with the above solution and allow to dry.

**Procedure.** Add a few drops of the reagent to the neutral solution to be tested, and make acid with 1.0 N hydrochloric acid. A dark red to violet color appears if molybdenum is present.

If the molybdenum solution is very dilute, the colored product adheres to the suspension of cetyl alcohol. By the above method 0.0005 mg. of molybdenum per ml. may be detected. The limit of detection is 1:2,000,000.

A spot test is carried out as follows:

**Procedure.** Place a drop of a neutral unknown solution on a freshly prepared strip of potassium cetyl xanthate paper, and expose it to the fumes of hydrochloric acid. A dark violet spot appears if molybdenum is present. As little as 0.0001 mg. of molybdenum in 0.05 ml. of solution gives this test.

The effect of inorganic salts upon this reaction is insignificant. Tungsten gives no color, but solutions with high tungsten content must be strongly acid to insure complete solution of molybdenum and tungsten. As little as 0.01 mg. of molybdenum may be detected in the presence of 0.5 g. of tungsten in 5 ml. of water.

1. J. V. Tamchyna, *Chem. Listy*, **24**, 465-6 (1930); *C.A.* **25**, 2661 (1931).
2. J. V. Tamchyna, *Mikrochemie*, **9**, 935 (1931); *C.A.* **25**, 2935 (1931).

## POTASSIUM METHYLXANTHATE

Synonym: Methyl potassium xanthate

$C_2H_3OS_2K$

Mol. Wt. 146.26

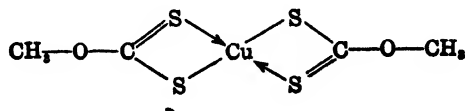
Beil. Ref. III, 208(83).

$CH_3-O-CSSK$

**Use:** Detection of arsenic, bismuth, cobalt, copper, molybdenum, nickel and tellurium.

**Preparation:** Potassium methylxanthate is prepared by the action of potassium methoxide, or a solution of potassium hydroxide in methyl alcohol, upon carbon disulfide (see potassium xanthate).<sup>1</sup>

**Reactions.** Potassium methylxanthate, like the ethyl compound, reacts with molybdenum, copper, cobalt, nickel, bismuth, arsenic and tellurium. The copper salt is represented by the following formula:



For the detection of the above substances, see section on potassium xanthate.

**Detection of nickel.** del Campo y Cerdan and Ferrer<sup>2,3</sup> recommend potassium methylxanthate as the most suitable of the xanthates for the differentiation of nickel and cobalt. To detect nickel in the presence of cobalt proceed as follows:

**Procedure.** Make the solution to be tested slightly acid with acetic acid, and to 2 ml. of this mixture add carefully by pouring down the side of the test tube, 1 ml. of a 1:1,000 solution of potassium methylxanthate in water. If nickel is present, a crystalline precipitate appears immediately, while the cobalt compound is colloidal and forms only slowly. In the presence of nickel, a yellow zone first forms, and in the presence of cobalt, and on further addition of potassium methylxanthate, a green color appears.

To detect cobalt in the presence of nickel, use a 5 per cent solution of potassium methylxanthate and proceed as above. An excess of the reagent should be added in order to precipitate all nickel. A green color indicates the presence of cobalt. If no green color forms, add a 3:100 solution of ammonium hydroxide to dissolve any nickel precipitate. A green precipitate remains if cobalt is present. Potassium methylxanthate is said to be about as sensitive as dimethylglyoxime for detecting nickel, and about as sensitive as Vogel's test for the detection of cobalt.

1. Zeise, *Ann.* **62**, 375.
2. A. del Campo y Cerdan and J. Ferrer, *Anales soc. espan. fis. quim.* **9**, 201-13, 272-6 (1911).
3. A. del Campo y Cerdan and J. Ferrer, *Rev. real. acad. cien. Madrid.* **9**, 979-95; *C.A.* **6**, 462 (1912).

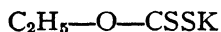
## POTASSIUM XANTHATE

Synonym: Ethyl potassium xanthate, potassium ethyldithiocarbonate, potassium ethylxanthogenate, potassium ethyl xanthate



Mol. Wt. 160.23

Beil. Ref. III, 209.



**Use:** Detection of arsenic, cobalt, copper, molybdenum, nickel, rhenium and tellurium.

Determination of arsenic, cobalt, copper, molybdenum and nickel.

Potassium xanthate consists of pale yellow crystals which are very soluble in water and soluble in alcohol. The aqueous solution is strongly alkaline. Store in a tightly closed bottle and protect from light.

**Preparation:** Add 5 g. of potassium hydroxide to 25 ml. of ethyl alcohol. Warm gently until no more potassium hydroxide dissolves. Cool and decant the clear supernatant liquid. Add 10 ml. of carbon disulfide and shake vigorously in a stoppered flask. Cool the flask and contents in ice water until the



potassium xanthate has completely separated, and while still cold add sufficient ether to dissolve any unreacted alcohol and carbon disulfide. Filter on a Buchner funnel and suck as dry as possible. Wash thoroughly with ether and spread on a sheet of filter paper until the ether has evaporated. Store in a stoppered bottle.<sup>1,2</sup>

**Detection and determination of copper.** Potassium xanthate reacts with very dilute solutions of copper salts to produce a yellow color which may be used for the detection<sup>3,55</sup> and colorimetric estimation of copper. The following test has been proposed by Korenman and Anflov:<sup>65</sup>

**Procedure.** Shake the solution containing copper with ethyl ether in the presence of a little potassium xanthate and ammonium hydroxide. A yellow color or precipitate in the ether layer shows the presence of copper. As little as 5% of copper can be detected in 5 ml. of solution by this method.

This reaction was first proposed by Scott and Derby<sup>4</sup> for the detection of copper, and was later applied by Supplee and Bellis<sup>5</sup> to the colorimetric determination of copper. According to Scott the test should be carried out in a neutral or slightly acid solution. Lampitt and co-workers<sup>6</sup> have found that if the solution is either slightly acid or slightly basic an opalescence appears, and this is thought to be due to the precipitation of copper xanthate or possibly sulfur. Despite these claims, Drabkin and Waggoner<sup>7</sup> report that the solution should be adjusted to pH 3.8, since under these conditions the maximum color is developed. It appears that with 0.02 mg. of copper for each 25 ml. of solution, a pH of 7.0-8.5 is most suitable, although a turbidity develops on standing. With 5 mg. of copper per 25 ml. of solution no precipitation occurs at pH 3.0-3.5, while a rapid precipitation occurs above pH 5.2. In general then, with 0.005-0.020 mg. of copper present per 25 ml. of solution, a pH of 7.0 appears to be most satisfactory. Further, the color comparison should be made within 15 minutes.<sup>10</sup>

The following procedure may be applied to very dilute solutions containing copper.

**Reagents.** *Potassium xanthate solution:* Dissolve 1 g. of pure potassium xanthate in a liter of water. Store the solution in an amber-colored glass stoppered bottle.

*Standard copper solution:* Dissolve 0.3928 g. of pure copper sulfate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) in a little water and dilute to 1 liter with thorough mixing. One ml. of this solution contains 0.1 mg. of copper.

**Procedure.** To a sample containing not more than 0.001 g. of copper, dissolved in water, add water to make the total volume 90 ml. and add 10 ml. of the potassium xanthate reagent. Compare the resulting yellow color with that produced with the standard. If the determination is to be made by the duplication method, the standard is prepared by adding 10 ml. of the potassium xanthate solution to 60 ml. of water, and then adding the standard copper

solution until the colors match after the volume of the sample and standard have been made the same.

To match the color by dilution or balancing, dilute 10 ml. of the standard copper solution to 500 ml. with water and 10 ml. of the potassium xanthate solution. This solution has a copper content of 0.002 mg. per ml.

Small quantities of lead, iron, cobalt, nickel, manganese and zinc do not interfere with this test. Iron interferes, however, and suitable steps must be taken to eliminate this interference. Drabkin and Waggoner<sup>7</sup> have found that the addition of sodium pyrophosphate removes interference due to iron, since sodium pyrophosphate does not react with xanthate unless more than 0.2 mg. is present. Elvehjem and Hart,<sup>8</sup> however, say that the use of pyrophosphate may lead to serious loss of copper unless temperature and pH are carefully controlled.

Nickel gives a color very similar to that with copper if present in suitable quantity.<sup>9</sup> The use of brass burners may also introduce appreciable quantities of copper. Copper-free distilled water should be used throughout the entire analysis.

King and Etzel<sup>9</sup> report that a fresh reagent should be prepared every few days, and the dry salt should be recrystallized every few weeks; otherwise a faint cloudiness may interfere with the determination. Conn and co-workers<sup>10</sup> say that high results obtained using the method of Supplee and Bellis<sup>5</sup> and King and Etzel<sup>9</sup> and Quam and Hellwig<sup>11</sup> are due to contamination from the porcelain crucible used in the determination.

Copper in both organic and inorganic materials may be determined by means of potassium xanthate, although the most important applications have been to the determination of copper in milk<sup>5,6,9-14</sup> and other biological materials.<sup>15-19</sup> Partridge<sup>50</sup> has used potassium ethyl xanthate for the determination of copper in aluminum alloys.

For the determination of copper in organic matter, the sample must be prepared by one of two methods described by Ansbacher and co-workers:<sup>15</sup>

(a) *Preparation by wet digestion*: Place the sample in a Kjeldahl flask and close the mouth with a funnel to prevent possible contamination. Add sufficient water to moisten the sample thoroughly and then add 15 ml. of concentrated sulfuric acid. Heat until the material turns black and fumes of sulfur trioxide are evolved, and then allow to cool. Add not more than 5 ml. of 20 per cent perchloric acid and 2 ml. of fuming nitric acid. There must be at least 5 ml. of sulfuric acid present when the perchloric acid is added. Heat the mixture with a small flame until oxides of nitrogen are no longer evolved, and then heat more strongly until fumes of sulfur trioxide appear. Allow to cool. If the solution is not colorless, add more perchloric acid and nitric acid and heat as described above.

Wash the colorless solution into an Erlenmeyer flask and dilute with water until the sulfuric acid content is less than 15 per cent by volume. Heat to boiling and add a few drops of concentrated nitric acid. Then pass hydrogen sulfide through the solution until it is cold. Allow the precipitate to settle and filter through a filtering crucible which has a porous bottom. Wash the pre-

precipitate with a 1 per cent acetic acid solution saturated with hydrogen sulfide until the washings no longer give a test for iron. Avoid exposing the copper sulfide to air for any length of time. Support the crucible on a glass triangle over a glass crystallizing dish and place this on a boiling water bath. Add 1 ml. of fuming nitric acid to the crucible, and when the liquid has all passed through, wash with 2 ml. of water. Allow to stand for some time on a water-bath until the solution has evaporated to dryness, and then place on a hot plate until acid fumes are no longer evolved. Care should be taken to avoid decomposition of the copper nitrate. Dissolve the residue in water, transfer to a volumetric flask, and dilute to a definite volume, depending upon the probable copper content.

This solution is then analyzed according to the above procedure.

(b) *Preparation by dry ashing:* Place the sample in a silica dish and heat on a hot plate until it is charred. Then place in an electric muffle and heat at a temperature not exceeding 400° C. for one half hour. Remove the dish and allow to cool. Add 2 ml. of fuming nitric acid, and if this does not wet the ash completely, add more. Evaporate to dryness on a hot plate, and repeat the nitric acid treatment and evaporation if only a trace of organic matter remains.

If a considerable quantity of organic matter remains after the first evaporation with nitric acid, again heat the sample in a muffle at 400° C. for 30 minutes. Remove, again add nitric acid and repeat the evaporation as described above. Repeat this series of operations as often as necessary until all carbon has been completely removed.

Add 10 ml. of concentrated sulfuric acid to the ash and heat. Cool, add 25 ml. of water, and transfer to an Erlenmeyer flask with 35 ml. of water, and then proceed exactly as described with the wet digestion method by heating to boiling, adding a few drops of concentrated nitric acid, and treating with hydrogen sulfide.

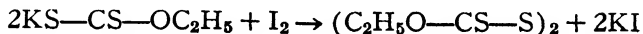
Smith<sup>20,21</sup> has used potassium xanthate for the determination of copper in textile materials:

**Procedure.** Place 10 g. of the sample in a Kjeldahl flask with 2.5 ml. of fuming nitric acid, 2.5 g. of sodium sulfate and 2.5 g. of potassium sulfate. As soon as the reaction has ceased, add 13 ml. of concentrated sulfuric acid and complete the digestion. Dissolve the residue in water and add 1:1 ammonium hydroxide until the mixture is just acid to Congo red. Add 5 ml. of 10 per cent phosphoric acid and dilute to 200 ml. Treat this solution as described above for the determination of copper.

Callan and Henderson<sup>15</sup> state that the xanthate method for copper is more sensitive than that with ferrocyanide, but they claim that the yellow color is not particularly suitable for matching especially when the amount of copper is very small. Elvehjem and Lindow<sup>16</sup> claim that the xanthate method is not sufficiently accurate for estimating copper in all kinds of biological materials.

Rupp and Kraus<sup>22</sup> have determined copper iodometrically after precipitation as copper xanthate. The determination is an indirect one based upon the

conversion of potassium xanthate to ethyldioxysulfocarbonate by iodine according to the reaction observed by Gastine:<sup>23</sup>



from this equation it may be seen that 2 moles of the xanthate are equivalent to 1 mole of iodine.

Oddo<sup>24</sup> has also determined copper titrimetrically by means of potassium xanthate. When a solution of a copper salt is added to a solution of potassium xanthate containing *s*-diphenylcarbazine, a yellow precipitate is formed until an excess of copper is present, and then a red color appears due to the reaction with *s*-diphenylcarbazine (indicator). Best results are obtained by adding an excess of 0.1 N potassium xanthate to the copper solution, then adding the indicator, and finally determining the excess xanthate with a standard copper solution by titrating to the appearance of a red color.

Potassium xanthate is also used for the precipitation of copper in separation procedures. Thus, in a dilute, slightly ammoniacal solution containing copper and nickel, copper xanthate is precipitated while nickel remains in solution as the complex ammine. Nickel can then be precipitated with dimethylglyoxime. For solutions containing 2 mg. of copper and 2 mg. of nickel, the greatest error observed in a series of determinations was 0.012 mg. of copper and 0.011 mg. of nickel.<sup>57</sup> Copper and zinc are separated by a similar procedure.<sup>60</sup>

**Detection of molybdenum.** Molybdates react with potassium xanthate in solutions of mineral acids to give a red to reddish-blue coloration. With large quantities of molybdenum an almost black oily liquid may separate from the solution. This reaction was first observed by Sievert,<sup>25,26</sup> and was later developed qualitatively by Malowan<sup>27,28</sup> and Koppel<sup>29,30</sup> as a sensitive test for molybdates. In organic solvents such as benzene, carbon disulfide and chloroform, the soluble complex  $\text{MoO}_3 \cdot [\text{SC}(\text{SH})(\text{OC}_2\text{H}_5)]_2$  is formed.<sup>25,30,31</sup> Malowan<sup>28</sup> found that the replacement of the ethyl radical in the xanthic acid makes the compound less sensitive toward molybdenum. Moreover, the substitution of organic groups for the hydrogen of xanthic acid also tends to prevent colorations with molybdc acid.

Koppel<sup>30</sup> reports that the xanthate test is satisfactory in the presence of hydrochloric, sulfuric and nitric acid, but is quite weak in solutions containing phosphoric, oxalic and acetic acid. When oxalic acid, tartaric acid or citric acid is added to an ammonium molybdate solution containing potassium xanthate, no color is produced. The addition of hydrochloric acid is sufficient to bring out the color from a tartrate solution, but not from an oxalate solution.

Bismuth, copper, cobalt, nickel and iron interfere only slightly with the molybdenum test, but more satisfactory results are obtained if these metals are removed prior to the test. Tungstate interferes if present in large quantities. Chromium if present should be in the chromic state.<sup>33</sup>

The following procedure is used to detect molybdenum:

**Procedure.** Place a drop of a nearly neutral or a slightly acid solution to be tested on a spot plate and mix with a small particle of solid potassium

xanthate. Then treat with 2 drops of 2 N hydrochloric acid. In this way as little as 0.04 $\gamma$  of molybdenum can be detected at a concentration of 1:1,250,000.

Clarke and Hermance<sup>32</sup> have studied the sensitivity of the xanthate reaction for molybdenum and report that only 0.2 $\gamma$  of molybdenum can be detected by a drop reaction. By impregnating paper with a solution of zinc xanthate, however, and employing a special technique, as little as 0.01 $\gamma$  of molybdenum can be detected. Rice and Yerkes<sup>33</sup> report that by applying the test to a solution of molybdate, only 4 mg. of molybdenum can be detected, but that this reaction can be made ten times as sensitive by extracting the color of the molybdenum complex with ether.

Leiba and Shapiro<sup>34</sup> describe the following method for detecting molybdenum in steel:

**Procedure.** On the surface of the steel to be tested place 1 drop of a solution prepared by dissolving 2 g. of bromine and 4 g. of potassium bromide in 10 ml. of water, and then allow to stand until the bromine is decolorized. Take up the drop with a strip of filter paper, and moisten the spot with a drop of 20 per cent sulfuric acid. After 2-3 minutes, add a drop of 2 per cent potassium xanthate solution. A red color appears if molybdenum is present. This test is sensitive to 0.5 $\gamma$  of molybdenum.

For steels containing less than 0.3 per cent of molybdenum, treatment with the bromine solution should be repeated two times. Thanheiser and Waterkamp<sup>35</sup> have used a similar method for detecting molybdenum in steel.

Tungsten gives no color with potassium xanthate, but solutions having high tungsten content must be made strongly acid while applying the molybdenum test in order to insure complete solution of molybdenum and tungsten.<sup>36</sup> Korenman and Tardov<sup>37</sup> describe the following test for detecting molybdenum in the presence of tungsten and vanadium:

**Procedure.** Carry out the following test in a test tube provided with a stop cock at the bottom. Place 5 ml. of the solution to be tested in this tube and acidify with 1 ml. of 2 N hydrochloric acid. Add a little potassium xanthate and then add 0.5-1.0 ml. of ether. Shake well. The xanthate complexes of molybdenum, iron, nickel, cobalt, and copper pass into the ether layer coloring it almost black. Withdraw the aqueous layer at the bottom, and to the ether layer add 1-2 ml. of 2 N sodium hydroxide and shake well. The hydroxides of the heavy metals precipitate and collect in the zone between the water and ether layers, while molybdenum and the xanthate salts pass into the aqueous layer as sodium salts. Filter the aqueous solution through a small filter and acidify the filtrate with 2 N hydrochloric acid. In the presence of molybdenum, a pink or a reddish-violet coloration appears. In the absence of molybdenum, the solution remains colorless.

By the above procedure it is possible to detect molybdenum in the presence of large quantities of tungsten and vanadium. Agte and co-workers<sup>38</sup> have used potassium xanthate for the detection of traces of molybdenum in tungsten ores,

and Grosset<sup>39</sup> employs the reagent for detecting molybdenum in a systematic scheme of analysis.

**Determination of molybdenum.** Potassium xanthate reacts with molybdenum in a strongly acid solution to form a red-violet color, the intensity of which is proportional to the molybdenum concentration. Pavelka and Laghi<sup>61</sup> recommended a pH of 1.8-1.9 for the color reaction. Thus molybdenum may be determined colorimetrically by extracting the red color with a mixture of petroleum ether and ethyl ether or with chloroform, and comparing by the usual methods.<sup>27,28,40,41</sup> The method is accurate to about 8 per cent, but error may result due to the volatility of the organic solvent and the instability of the molybdenum compound. Gillis<sup>62</sup> recommends the xanthate method.

**Reagent.** Prepare 100 ml. of a saturated solution of potassium hydroxide in absolute alcohol and then shake with an excess of carbon disulfide until no further reaction occurs. Allow a small quantity of carbon disulfide to remain in the vessel to insure saturation.

**Procedure.** To a solution of the sample add 0.2 N sodium hydroxide until the mixture is faintly alkaline, and then add 5 ml. of the reagent. Mix well and add 30 per cent acetic acid until distinctly acid. Extract with 25 ml. of a mixture of 35 per cent petroleum ether and 65 per cent ethyl ether. Repeat the extraction with a second 25-ml. portion of the solvent. Mix the two extracts and compare, by diluting with more of the solvent, with a standard prepared from a standard molybdenum solution similarly treated. Chloroform may be used for the extraction.

Panchenko<sup>42</sup> has used a similar method for the determination of molybdenum in special steel, and Leitmeier and Feigl<sup>43</sup> have applied the reaction to the determination of molybdenum in rocks and minerals.

Hall<sup>41</sup> has used potassium xanthate for the separation of molybdenum and tungsten:

**Procedure.** Neutralize the molybdenum solution with 0.2 N sodium hydroxide and add 0.5 g. of solid potassium xanthate, and then add several drops of 1:3 sulfuric acid. To insure the formation of a soluble metatungstate, add the acid dropwise with agitation of the solution after the addition of each drop until the curdy precipitate of tungstic acid has redissolved. After a certain point no quantity of acid causes the precipitation of tungsten from a cold solution. On the addition of acid a white turbidity appears due to the formation of molybdenum xanthate, but this turns red in a few seconds. Extract the red compound with chloroform and after the separation of the chloroform layer, wash several times with water. Continue the addition of potassium xanthate, acid, and chloroform until the chloroform layer remains colorless. Evaporate the molybdenum extract to dryness, dissolve the residue in nitric acid, and then determine molybdenum by any of the well-known methods.

The separation of molybdenum from iron, nickel, vanadium and uranium by a similar method proved unsuccessful. Contrary to Malowan's claim, Hall<sup>41</sup>

has found that iron, nickel, vanadium and uranium form colored compounds with potassium xanthate under the same conditions as molybdenum, and he further reports that these are soluble in chloroform.

**Detection and determination of nickel and cobalt.** An aqueous solution of potassium xanthate produces a yellow color or precipitate with solutions of nickel salts, and this does not disappear upon treatment with ammonium hydroxide.<sup>44</sup> Phipson<sup>45</sup> and Compin<sup>46,47</sup> have used this reaction for the detection of nickel, and to distinguish between nickel and cobalt.

Compin<sup>46,47</sup> has also used potassium xanthate for the determination of cobalt in presence of nickel. This procedure is based upon the relative solubility of the xanthates of these metals in ammonium hydroxide. The following procedure is used to determine cobalt in analysis of nickel salts:

**Procedure.** To a few ml. of a 10 per cent solution of the nickel salt to be analyzed, add 2 drops of hydrochloric acid, and then add dropwise sufficient freshly prepared 5 per cent potassium xanthate solution to precipitate all the metals. Avoid a large excess of the reagent. A voluminous brown precipitate of nickel xanthate is formed. Add an equal volume of ammonium hydroxide, which dissolves the nickel compound instantly giving a blue colored solution. If cobalt is present in a concentration approximating 1:2000, green granules of cobalt xanthate may be observed. The extraction of the cobalt compound with ether gives a green colored ether layer. This constitutes a satisfactory qualitative test for 0.01 mg. of cobalt in 5 ml. of solution. The presence of iron may mask the green color, but this trouble can be eliminated by using as a standard for comparison a nickel salt free from both iron and cobalt. The above reaction can be used for the quantitative separation of nickel and cobalt by filtering the cobalt xanthate from the ammoniacal solution. The precipitate is converted to cobalt sulfate in the usual manner and weighed in that form.

An error sometimes results in using this method due to the occasional formation of a cobalt salt which is somewhat soluble in ammonium hydroxide. This can be overcome by carefully adding hydrochloric acid, again precipitating the xanthates and finally redissolving nickel xanthate with ammonium hydroxide. The accuracy obtained in determining nearly equal quantities of nickel and cobalt is about 4 per cent for nickel and 1-2 per cent for cobalt.

Whitby and Beardwood<sup>48</sup> have used a somewhat similar method for separating nickel from copper and cobalt.

**Procedure.** To a solution containing nickel and cobalt, add 1 g. of citric acid and an excess of ammonium hydroxide. Then add 1 g. of potassium xanthate and sufficient acetic acid to precipitate the xanthates of nickel and cobalt. Allow the mixture to stand for three hours at a temperature just below boiling. Then filter and wash the precipitate with hot water. Return the precipitate to the beaker in which the initial precipitation was carried out, and treat with approximately 8 N ammonium hydroxide. Heat on a water-bath, filter, and wash with dilute ammonium hydroxide until the filtrate shows no trace of a yellow color. The nickel is contained in the filtrate and cobalt remains on the

paper. Nickel can be precipitated in the filtrate by acidifying with acetic acid. By igniting the precipitates to a full red heat in a muffle which is provided with a free access of air, the precipitates are converted to  $\text{Co}_3\text{O}_4$  and  $\text{NiO}$ , in which forms they may be weighed.

Copper behaves like cobalt in the above determination. The copper precipitate is weighed as  $\text{CuO}$ . Ferric iron and arsenic do not interfere with the separation.

Campbell and Andrews<sup>49</sup> recommend the following procedure for separating nickel and iron:

**Procedure.** To a solution containing nickel and iron, add nitric acid until a 20-25 per cent excess of the acid is present, and then add sodium pyrophosphate dissolved in warm water. The amount of pyrophosphate required is determined by the ratio of 13 g. of the salt to each 1 g. of metal present. Dissolve the white precipitate of ferric pyrophosphate by the cautious addition of a clear, moderately concentrated solution of sodium carbonate with thorough agitation until the precipitate just dissolves and the solution is dull olive-green in color. Carefully avoid an excess of sodium carbonate.

Filter through asbestos into a 500-ml. flask, and precipitate nickel by the addition to the cold solution of 2 g. of potassium xanthate, freshly dissolved in a little water. Stopper the flask and shake it at frequent intervals for 10 minutes. Filter through asbestos and immediately wash the precipitate with a freshly prepared 1 per cent solution of potassium xanthate. Dissolve the precipitate with a small amount of freshly diluted fuming nitric acid (1:1). Add 2 ml. of sulfuric acid, previously diluted with a little water, and evaporate until all nitric acid is expelled and fumes of sulfur trioxide appear. Dissolve the nickel sulfate in a small quantity of water, and precipitate any accompanying iron with ammonium hydroxide. Filter, dissolve the precipitate with a little dilute sulfuric acid, reprecipitate with ammonium hydroxide and filter. Combine the first and the second filtrate. The nickel may then be determined in the filtrate either electrolytically or titrimetrically.

Ahrens<sup>58</sup> has described a method for the determination of cobalt in minerals using a preliminary separation with potassium xanthate. Cobalt is precipitated along with copper as the xanthate, and, after dissolving the precipitate in aqua regia and fuming with nitric and sulfuric acids, the cobalt is titrated potentiometrically in an ammoniacal solution buffered with ammonium citrate with a standard solution of potassium ferricyanide.

**Detection of tellurium.** Unlike selenium, tellurium is not liberated by thiourea from neutral or acid solutions. A yellow crystalline compound is precipitated when thiourea is added to a concentrated solution containing tellurium, and this compound is insoluble in the usual organic solvents except ethyl alcohol. If the yellow reaction mixture is shaken with ether and potassium xanthate, the ether layer first turns a mahogany red, and finally a black precipitate forms and the aqueous layer becomes colorless. Selenium gives no coloration.<sup>50</sup> If molybdenum is present it may color the ether layer and mask the color of tel-



lurium, but the addition of ammonia causes the disappearance of the molybdenum color and the formation of the black turbidity or precipitate with tellurium. By repeated extractions with ether containing potassium xanthate, it is possible to effect a quantitative separation of tellurium.

**Detection and determination of arsenic.** Arsenic xanthate is formed when powdered potassium xanthate, suspended in an excess of carbon disulfide, is allowed to act upon arsenic trichloride. The arsenic is precipitated quantitatively by allowing the mixture of arsenic chloride and potassium xanthate to stand 15 minutes, then adding water if necessary, and finally acidifying with glacial acetic acid. A white precipitate of the arsenic compound forms. The arsenic compound has the formula  $\text{As}(\text{SCSOC}_2\text{H}_5)_3$ . Arsenic may be determined in this compound by any of the general methods.

If only a small quantity of arsenic is present, the arsenic chloride-potassium xanthate mixture is shaken with chloroform, and the chloroform layer is then evaporated and examined microscopically for the arsenic compound.<sup>51</sup>

Trivalent arsenic is extracted as the xanthate by carbon tetrachloride from an acid solution.<sup>50</sup> Antimony and other metal xanthates which are also extracted may be removed from the carbon tetrachloride solution by washing with concentrated hydrochloric acid containing stannous chloride. Arsenic xanthate is not affected by this treatment. Aluminum, manganese, lead, cadmium, mercury, bismuth and zinc do not interfere.

**Detection of rhenium.** If solutions containing molybdenum and rhenium are treated with potassium xanthate, and the molybdenum complex first removed with chloroform, rhenium can be detected with fair accuracy in the remaining solution. Iron and copper interfere. Oxidizing agents, large quantities of reducing agents and high salt concentration cause erratic results.<sup>52,53</sup>

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**XANTHOGENEAMIDE** $C_8H_7ONS$ 

Mol. Wt. 105.15

Beil. Ref. III, 137(63).

**Use:** Detection of copper.

Xanthogeneamide is a crystalline solid melting at 40-41° C. It is only slightly soluble in water.

**Preparation:** Xanthogeneamide is prepared by passing a stream of dry ammonia into an alcoholic solution of ethyl xanthate, and allowing the mixture to stand 24 hours. The mixture is then distilled and the residue evaporated to dryness on a water bath. The product is dried over sulfuric acid for several days.<sup>1</sup>

**Detection of copper.** Copper may be detected by the red color which is obtained when xanthogeneamide is added to a solution of a copper salt.<sup>2</sup>

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## CHAPTER V

### MISCELLANEOUS SULFUR COMPOUNDS

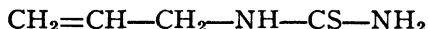
#### ALLYLTHIOUREA

Synonym: Thiosinamine

$C_4H_8N_2S$

Mol. Wt. 116.18

Beil. Ref. IV, 211.



**Use:** Detection of cadmium and uranium.

Allylthiourea is a crystalline solid which melts at 70-71.5° C. It is readily soluble in water, and in alcohol, but is only slightly soluble in ether and is insoluble in benzene.

**Preparation:** Mix equal parts of allylthiocyanate and absolute alcohol, and add this mixture to an equal quantity of 30 per cent ammonia. Warm with shaking almost to boiling and then evaporate on a water-bath. Separate the almost pure product and recrystallize from alcohol.<sup>1</sup>

**Detection of cadmium and uranium.** A persistent yellow precipitate is obtained by boiling an alkaline solution of allylthiourea with a little uranium or cadmium. No other heavy metals or alkali or alkaline earth metals yield a precipitate with this reagent. The reagent is a 5 per cent solution of allylthiourea to which, just before use, 5 per cent of a 30 per cent solution of sodium hydroxide is added. On adding 2-3 drops of the solution to be tested to 4 ml. of the reagent, a yellow precipitate forms if cadmium or uranium is present.<sup>2-4</sup>

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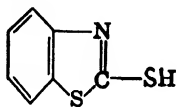
#### 2-BENZOTHAIAZOLETHIOL

Synonym: Mercaptobenzothiazole

$C_7H_5NS_2$

Mol. Wt. 167.24

Beil. Ref. XXVII, 185(271).



**Use:** Detection of bismuth, cadmium, cobalt, copper, gold, lead, mercury, nickel, thallium and zinc.

2-Benzothiazolethiol occurs as white needles or crystalline leaflets. It melts at 179° C. It is insoluble in water, but is moderately soluble in alcohol, ether and glacial acetic acid, and is soluble in alkalis and in alkali carbonate solutions.

**Preparation:** Mix 1 part of azobenzene and 2.5 parts of carbon disulfide, and heat for 5 hours in a closed tube at 260-270° C. Open the tube, and after allowing the excess carbon disulfide to evaporate, moisten the residue with alcohol to facilitate further treatment with sodium hydroxide. Digest this mixture for a time with a moderately concentrated solution of sodium hydroxide, and dilute the mixture with a considerable quantity of water. Filter, and acidify the filtrate to precipitate impure 2-benzothiazolethiol. Filter and purify the precipitate by repeating the following process several times: Dissolve in warm sodium carbonate solution, digest with decolorizing charcoal, filter, and acidify; and then finally recrystallize several times from dilute alcohol.<sup>1</sup>

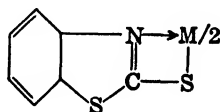
2-Benzothiazolethiol is a technical product sold as a rubber accelerator under the name of "Captax" or "Vulkacit-mercapto." The commercial product is purified by repeatedly precipitating from a sodium carbonate solution with hydrochloric acid.

**Reactions with metals.** 2-Benzothiazolethiol, which contains the acidic —SH group, reacts with solutions of metallic salts to form metallic derivatives in which the hydrogen of the —SH group is replaced by various metals. Kuras<sup>2,3</sup> has prepared and described a number of these salts which are given in Table 17.

TABLE 17.—METALLIC SALTS OF 2-BENZOTHAIOLETHIOL

Metal	Formula	Description
Copper .....	$\text{Cu}(\text{C}_7\text{H}_4\text{NS}_2)_2$	Pale orange-yellow
Lead .....	$\text{Pb}(\text{C}_7\text{H}_4\text{NS}_2)_2$	Lemon-yellow
Lead .....	$\text{Pb}(\text{OH})(\text{C}_7\text{H}_4\text{NS}_2)$	White
Bismuth .....	$\text{Bi}(\text{C}_7\text{H}_4\text{NS}_2)_3$	Chrome-yellow
Cadmium ....	$\text{Cd}(\text{NH}_3)_2(\text{C}_7\text{H}_4\text{NS}_2)_2 \cdot \text{H}_2\text{O}$	Unstable, crystal white
Cadmium ....	$\text{Cd}(\text{C}_7\text{H}_4\text{NS}_2)_2$	White and crystalline
Nickel .....	$\text{Ni}(\text{C}_7\text{H}_4\text{NS}_2)_2$	Brown, sparkling microcrystals
Mercury ....	$\text{Hg}(\text{C}_7\text{H}_4\text{NS}_2)_2$	Yellow-white microcrystals
Gold .....	$\text{Au}(\text{C}_7\text{H}_4\text{NS}_2)_3$	Amorphous, yellow-white
Thallium ....	$\text{Te}(\text{C}_7\text{H}_4\text{NS}_2)_2$	Sulfur-yellow microcrystals
Cobalt .....	$\text{Co}_2(\text{OH})(\text{C}_7\text{H}_4\text{NS}_2)_3$	Green microcrystals
Zinc .....	$\text{Zn}_2(\text{OH})(\text{C}_7\text{H}_4\text{NS}_2)_3$	White microcrystals

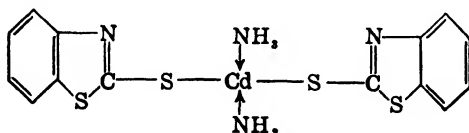
In most cases the structure of these salts appears to be that of complex internal salts as illustrated by the following formula:<sup>9</sup>



A number of these reactions may be applied with excellent results to the detection and determination of the various metals. A more complete description of these reactions follows:<sup>4</sup>

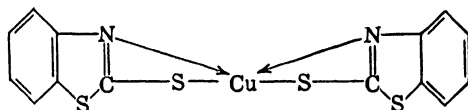
(a) *Bismuth*: Bismuth is quantitatively precipitated in the form of a yellow precipitate when an excess of an alcoholic solution of 2-benzothiazolethiol is added to a solution of a bismuth salt, which is then made slightly alkaline with ammonia.

(b) *Cadmium*: Ammoniacal solutions of the reagent give a white precipitate when added to ammoniacal solutions of cadmium salts. The following formula has been assigned to this compound.



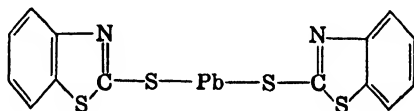
(c) *Cobalt and zinc*: Cobalt and zinc are precipitated by an alcoholic solution of reagent in presence of a little of acetic acid.

(d) *Copper*: An alcoholic solution of the reagent yields with copper an orange-yellow, flocculent precipitate from neutral, ammoniacal, or acetic acid solutions. Two moles of the reagent combine with 1 mole of copper to give a compound having the following composition.

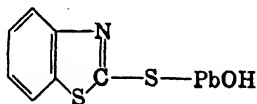


(e) *Gold*: A precipitate of  $\text{Au}(\text{C}_7\text{H}_4\text{NS}_2)_3$  is formed when an alcoholic solution of the reagent is added to a solution of a gold salt. Metallic gold may be formed by igniting the washed precipitate of the gold salt.

(f) *Lead*: Lead reacts with 2-benzothiazolethiol to form a yellow normal salt of the following composition.



Or a white basic salt having the following structure.



(g) *Mercury*: A yellowish-white precipitate is obtained when an alcoholic solution of reagent is added to a cold solution of mercuric acetate.

(h) *Nickel*: A brown precipitate, which is slightly soluble in water and alcohol, is formed when a hot alcoholic solution of the reagent is added to the filtrate obtained after filtering a hot alcoholic solution of sodium acetate and nickel acetate.

(i) *Thallium*: A yellow precipitate is obtained when an ammoniacal solution of the reagent is added to a cold solution containing a thallos salt.

**Determination of copper.** An alcoholic solution of 2-benzothiazolethiol gives with solutions of copper salts an orange yellow precipitate which can be filtered off and ignited to cupric oxide. This reaction is very sensitive and can be used for detection or determination of copper in the presence of nickel, cobalt, zinc, cadmium, magnesium, calcium, barium, and strontium.<sup>5,6</sup>

**Procedure.** Add an excess of a saturated (5 per cent) alcoholic solution of 2-benzothiazolethiol to the warm, neutral aqueous solution of the copper salt. If the solution to be analyzed is acid, neutralize with ammonium hydroxide. Heat the mixture, with continuous shaking, until the flocculent orange-yellow precipitate forms into balls and the liquid is clear. Filter while hot, wash the precipitate with hot water, and dry at 110-120° C. Finally burn the filter in a crucible, and ignite to constant weight, and weigh as CuO.

During the ignition of the copper precipitate to copper oxide, some copper sulfide or sulfate is formed. Springer<sup>11</sup> has shown that theoretical results can be obtained by experimentally determining the SO<sub>3</sub> content of the copper oxide residue and correcting the results, but in this case the procedure is too long to be of practical value.

**Determination of cadmium.** Cadmium is precipitated quantitatively when an ammoniacal solution of a cadmium salt is treated with an ammoniacal solution of 2-benzothiazolethiol. The precipitate as first formed contains two molecules of ammonia but these are expelled when the precipitate is dried at 110-120° C., and the dried precipitate is weighed as Cd(C<sub>7</sub>H<sub>4</sub>NS<sub>2</sub>)<sub>2</sub>.<sup>7</sup>

**Procedure.** Add ammonium hydroxide to the solution containing the cadmium salt until the mixture is clear, and then add an ammoniacal solution of 2-benzothiazolethiol in excess. A thick, milky-white turbidity appears at once, and this on shaking or with slight warming turns to an abundant white, crystalline precipitate. Filter through a filtering crucible, wash with dilute ammonia, dry at 110-120° C. to constant weight. From the weight of the precipitate, calculate the percentage of cadmium in the material to be analyzed by using the following formula.

$$\text{Per cent Cd} = \frac{25.30 \times \text{wt. of residue}}{\text{wt. of sample}}$$

**Determination of copper and cadmium in the presence of one another.** The following procedure may be used to determine copper and cadmium when they are present in the same solution: <sup>7</sup>

**Procedure.** In a neutral solution, precipitate copper with an excess of an alcoholic solution of 2-benzothiazolethiol, and then filter, wash with hot water, dry, ash, ignite and weigh as described in the procedure for copper. To the hot filtrate, add an excess of ammonia and shake well. If a precipitate of

the cadmium salt does not form, add a few ml. of an ammoniacal solution of the reagent, and proceed as in the preceding section.

**Determination of lead.** 2-Benzothiazolethiol reacts with solutions of lead salts to precipitate quantitatively the normal salt ( $\text{Pb}(\text{C}_7\text{H}_4\text{NS}_2)_2$ ) and a white, basic salt ( $\text{Pb}(\text{C}_7\text{H}_4\text{NS}_2)(\text{OH})$ ). The basic salt is precipitated from a hot neutral solution as a white, needle-like crystalline precipitate, which can be weighed as such after drying at  $110^\circ\text{C}$ . The normal salt, which is obtained by precipitation from a cold solution, is never formula pure, but always contains some basic salt. By boiling with concentrated ammonium hydroxide, the normal salt is completely changed to the basic salt. The following procedure serves as a satisfactory method for the gravimetric determination of lead.<sup>8</sup>

**Procedure.** Heat the neutral, aqueous solution containing about 0.1 g. of lead nitrate, almost to boiling, and add dropwise a slight excess of a reagent prepared by dissolving 1 g. of 2-benzothiazolethiol in 100 ml. of 2.5 per cent ammonia. About 20 ml. of the reagent is necessary for 0.1 g. of lead nitrate. Filter the precipitate which forms, wash with 2.5 per cent ammonia, and dry at  $110^\circ\text{C}$ . and weigh. The factor for lead is 0.5309.

**Determination of thallium.** The yellow precipitate of  $\text{Tl}(\text{C}_7\text{H}_4\text{NS}_2)$  is appreciably soluble in water, and so in the determination of thallium by precipitation in this form it is necessary to avoid excessive dilutions and to use at least three times the theoretical quantity of the precipitant. The following method may be used to determine thallium gravimetrically.<sup>8</sup>

**Procedure.** To 30 ml. of a cold solution containing about 0.1 g. of a thallous salt, add dropwise a 1 per cent solution of a 2-benzothiazolethiol in 2.5 per cent ammonia until a three-fold excess is present. Filter the precipitate and wash with 30 ml. of a cold 2.5 per cent ammonia solution. Dry at  $110^\circ\text{C}$ . and weigh. The factor for thallium is 0.5517.

**Determination of bismuth.** The yellow precipitate of  $\text{Bi}(\text{C}_7\text{H}_4\text{NS}_2)_3$ , which is formed when 2-benzothiazolethiol is added to a solution of a bismuth salt, is always contaminated with a little bismuth hydroxide, so that the precipitate can not be weighed as such, but can be weighed only after ignition to  $\text{Bi}_2\text{O}_3$ . With this precaution, however, 2-benzothiazolethiol may be used satisfactorily for the determination of bismuth.<sup>8</sup>

**Procedure.** Add an excess of a 1 per cent solution of 2-benzothiazolethiol in 2.5 per cent ammonia to a solution of a bismuth salt, and then add sufficient ammonia to make the solution slightly ammoniacal. Heat the mixture until the precipitate is coagulated, and filter through ashless filter paper. Wash the precipitate with a freshly prepared 2.5 per cent ammonia solution containing 0.5 per cent of the reagent, and dry at  $110^\circ\text{C}$ . Separate the precipitate from the paper as completely as possible, and dissolve the residue in a little hot dilute nitric acid, collecting the resulting solution in a weighed porcelain crucible. To this solution, add the principal portion of the precipitate and eva-



porate to dryness. Finally ignite to  $\text{Bi}_2\text{O}_3$  and weigh. Results are within 0.2 mg. of the actual value.

**Determination of gold.** Gold is quantitatively precipitated as  $\text{Au}(\text{C}_7\text{H}_4\text{NS}_2)_3$  by adding the reagent to a solution of a gold salt. Gold may be determined gravimetrically after precipitation by igniting the precipitate to metallic gold, which is then weighed.<sup>8</sup>

**Procedure.** The formation of insoluble  $\text{Au}(\text{C}_7\text{H}_4\text{NS}_2)_3$  is best accomplished by adding an alcoholic solution of the reagent to a solution of a gold salt. After the formation of the precipitate, remove the alcohol by evaporation, and recover the gold precipitate by filtration. Then carefully wash the precipitate with hot water and ignite, together with the filter, whereby metallic gold is formed. Any excess of the reagent, which usually accompanies the gold precipitate into the filter, is destroyed during the ignition. Excellent results are claimed for this method.

1. P. Jacobson and A. Frankenbacher, *Ber.* **24**, 1403 (1891).
2. M. Kuras, *Chem. Obzor.* **14**, 145-9 (1939); *C.A.* **33**, 9200 (1939).
3. M. Kuras, *Collection Czechoslov. Chem. Commun.* **11**, 367-76 (1939); *C.A.* **34**, 5788 (1940).
4. G. Spacu and M. Kuras, *J. prakt. Chem.* **144**, 106 (1935).
5. G. Spacu and M. Kuras, *Bul. soc. stiinte Cluj.* **8**, 243-4 (1935); *C.A.* **30**, 1683 (1936).
6. G. Spacu and M. Kuras, *Z. anal. Chem.* **102**, 24-8 (1935); *C.A.* **29**, 7213 (1935).
7. G. Spacu and M. Kuras, *Z. anal. Chem.* **102**, 108-10 (1935); *C.A.* **29**, 7213 (1935).
8. G. Spacu and M. Kuras, *Z. anal. Chem.* **104**, 88-93 (1936); *C.A.* **30**, 2875 (1936).
9. J. V. Dubsky, *Mikrochemie.* **28**, 145-72 (1940); *C.A.* **34**, 4686 (1940).
10. A. W. Hofmann, *Ber.* **20**, 2264 (1887).
11. L. Springer, *Dissertation, Techn. Hochschule Muenchen* 1913, p. 32.

## BENZYL PSEUDO THIOUREA

$\text{C}_8\text{H}_{10}\text{N}_2\text{S}$

Mol. Wt. 166.24

Beil. Ref. XII, 1051.



**Use:** Detection of free hydrochloric acid.

**Preparation:** Dissolve 76 g. of thiourea in 200 ml. of 40 per cent alcohol and add with constant stirring 126.5 g. of benzyl chloride. Warm gently until the reaction starts and then warm until no more hydrogen chloride is evolved. Cool and filter with suction the crystalline product which separates. Purify by recrystallizing from 40 per cent alcohol. The compound exists in two modifications: a stable form melting at  $144^\circ\text{C}$ . which solidifies to a metastable form melting at  $175^\circ\text{C}$ .<sup>1,2</sup>

**Detection of free hydrochloric acid.** Benzyl pseudo thiourea hydrochloride crystallizes on the object slide of a microscope in thin rhombs and tablets, whose acute angles are  $74^\circ\text{C}$ . When free hydrochloric acid is present, however, curious plates and prisms are obtained which may be used for the

microchemical detection of hydrochloric acid.<sup>3</sup> The reagent is prepared by dissolving 5 g. of benzyl pseudo thiourea in 50 ml. of water containing 1 ml. of concentrated hydrochloric acid.

1. A. Bernthsen and H. Klinger, *Ber.* 12, 574 (1879).
2. R. F. Chambers and P. C. Scherer, *Ind. Eng. Chem.* 16, 1272 (1924).
3. E. M. Chamot and C. W. Mason, *Handbook of Chemical Microscopy*, Vol. II. 2nd Ed., p. 423-4, John Wiley, New York, 1940.

#### 4-CHLORO-1,2-DIMERCAPTOBENZENE

$C_6H_5ClS_2$

Mol. Wt. 176.68

$Cl-C_6H_3(SH)_2$

**Use:** Detection and determination of tin.

4-Chloro-1,2-dimercaptobenzene is a white crystalline solid melting at 31° C. It boils at 165° C. at a pressure of 32.5 mm.

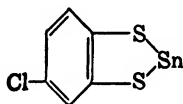
**Preparation.** *p*-Chloroanilinesulfonic acid: Heat 52 g. of *p*-chloroacetanilide (for preparation, see *p*-chloroaniline) and 30 g. of concentrated sulfuric acid in a dish and stir with a thermometer. The acetic acid boils away at 140-190° C. and the mass solidifies. Keep the temperature at 180° C. for about two hours, and then recrystallize from water containing a little charcoal.

*1-Chlorobenzene-3,4-disulfonylchloride*: Dissolve 83 g. of *p*-chloroaniline-sulfonic acid in 400 ml. of 1 N sodium hydroxide and 500 ml. of water, and add the resulting solution to 1000 g. of ice and 200 ml. of hydrochloric acid. Slowly shake 30 g. of solid sodium nitrite into the mixture and stir for 30 minutes, and then neutralize with 159 g. of sodium bicarbonate. Add 100 g. of potassium xanthate in 100 ml. of water and warm, and then evaporate to dryness. Extract the residue with alcohol and remove the alcohol on a water-bath, and then oxidize the residue with 240 ml. of nitric acid ( $d = 1.4$ ). Heat the mixture on a water-bath to remove the nitric acid, and then add 200 g. of barium chloride. Treat the resulting barium salt with sodium sulfate and filter, and evaporate the filtrate to dryness. Treat 170 g. of the sodium salt thus formed with 250 g. of phosphorous pentachloride and heat the mixture for 3 hours at 140° C. Pour the mixture onto ice and crystallize the solid which is formed as rapidly as possible from benzene. Finally wash with gasoline and dry.

*4-chloro-1,2-dimercaptobenzene*: Reduce 150 g. of the above sulfonyl chloride with 500 g. of tin and 1200 ml. of hydrochloric acid by boiling until nearly all the tin is dissolved. Cool the mixture by immersing the flask into a bath of ice water, and shake vigorously until the temperature has fallen to 70° C. Then add 200 ml. of benzene and filter rapidly. Extract the mother liquor with 50 ml. of benzene after the separation. Dry the benzene extracts with sodium sulfate and distill off the benzene. The residual oil distills at 165° C. at 32.5 mm. to give a colorless liquid which crystallizes on standing.

**Detection and determination of tin.** In 1936 Mills and Clark<sup>1</sup> prepared 4-chloro-1,2-dimercaptobenzene, and observed the red color which was formed with the tin used in one stage of the preparation. This suggested the use of 4-chloro-1,2-dimercaptobenzene as a reagent for the detection and colorimetric determination of small quantities of tin. This problem was later studied by Clark,<sup>2,3</sup> who found that no other element or compound gave a red color with the reagent under comparable conditions except bismuth, which yields a brick red precipitate quite unlike the compound formed with tin. The formation of red compounds with 4-chloro-1,2-dimercaptobenzene, and other 1,2-dimercaptobenzenes therefore seems to offer a fairly specific and sensitive test for tin. Tests such as those with cacotheline and the molybdenum blue reaction depend upon the reducing properties of stannous tin, and so their use is subject to some uncertainty due to the possible presence of many other reducing substances.

The formation of the red color with tin may be due to the fact that an atom of the metal forms a part of a 5-membered ring with the reagent:



The following procedure for detecting tin has been suggested by Clark.<sup>2,3</sup>

**Reagent.** The reagent is a 0.2 per cent solution of the compound in a dilute solution of sodium hydroxide. The compound readily oxidizes in air to form a white insoluble disulfide, and so the reagent solution must be stored in hydrogen or prepared just before use.

**Procedure.** Add a few drops of the reagent to an acid solution (which may contain as much as 15 per cent hydrochloric acid) containing tin and then warm. A pink or red color develops within a few seconds if tin is present in concentrations greater than 1:1,000,000.

A similar color is also obtained with solutions containing stannic salts, probably due to reduction by the reagent, but a longer time is required for the color to develop and the test is less sensitive. If, however, a little thioglycolic acid is added to the solution to be tested, all the tin is rapidly reduced, and the sensitivity of the test is then found to be independent of the initial state of oxidation of tin.

This method for detecting tin is particularly useful in a systematic scheme of qualitative analysis. Both antimony and arsenic may be present in the solution to be tested, although a yellow precipitate of the arsenic and antimony derivatives is formed first, but with tin a red color may be observed on adding an excess of the reagent. In general, 4-chloro-1,2-dimercaptobenzene may be used for testing tin in the presence of all other cations except those whose mercaptides have colors of sufficient intensity to mask that of tin. In the following list, any metal is precipitated by 4-chloro-1,2-dimercaptobenzene before

those which are placed after it when the reagent is added to an acid solution of the cation at the boiling point:

Silver .....	Yellow
Mercury .....	Pale yellow
Copper .....	Black
Bismuth .....	Brick red
Cadmium .....	Pale yellow
Arsenic .....	Pale yellow
Antimony .....	Yellow
Nickel .....	Black
Tin .....	Red
Cobalt .....	Black
Lead .....	Bright yellow

It will be seen, therefore, that with an excess of the reagent only copper, bismuth, and nickel are likely to interfere with the tin test.

**Colorimetric determination of tin.** Clark has studied the color reaction of 4-chloro-1,2-dimercaptobenzene and tin in the presence of thioglycolic acid, and has found that it is suitable for the colorimetric determination of very small quantities of tin. The following procedure is used:

**Procedure.** Add a drop of thioglycolic acid to the solution to be analyzed, and then dilute until the concentration of the tin lies between 1.5-6.0 p.p.m. Place 5-10 ml. of this solution in a test tube, and in a second test tube place an identical volume of a standard tin solution containing about 10 p.p.m. of tin containing a quantity of thioglycolic acid corresponding to 0.2 g. per liter. Add 0.5 ml. of hydrochloric acid to each tube and then an identical quantity of the reagent solution. This causes the immediate precipitation of the white reagent. Immerse both tubes in boiling water for 10 seconds to develop the color, and then slowly add distilled water to the tube containing the standard solution until the colors in the two tubes are matched. In this way tin can be determined with an accuracy of about 10 per cent.

Two per cent solutions of the following salts were found to be without effect upon the determination: ammonium chloride, sodium chloride, magnesium sulfate, zinc sulfate, calcium chloride, barium chloride, strontium chloride, potassium aluminum sulfate, potassium fluoride, potassium chloride, potassium bromide, potassium iodide, potassium cyanide, potassium thiocyanate, sodium tetraborate and sodium sulfite. Iron salts in concentrations as high as 2 per cent sometimes impart a slightly different tint to the color, but with concentrations as low as 0.5-1.0 per cent they are without appreciable effect. Manganous sulfate does not interfere in concentrations up to 1 per cent. A saturated solution of lead chloride does not interfere, provided as much as 7 per cent hydrochloric acid is present. Nitrites and phosphates must be absent.

Results obtained by this method are shown in Table 18.

TABLE 18.

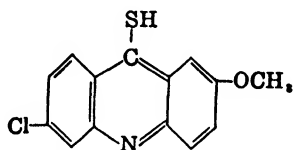
Tin Present p.p.m.	Tin Found p.p.m.
2.8	3.1
4.2	5.35
4.2	4.7
2.3	2.3
1.9	2.2
1.5	1.5
1.2	0.9

1. W. H. Mills and R. E. D. Clark, *J. Chem. Soc.* **139**, 175 (1936).
2. R. E. D. Clark, *Analyst*, **61**, 242-45 (1936).
3. R. E. D. Clark, *Tech. Pub. Intern. Tin Research Development Council Ser. A*, **41**, 7 pp. (1936); *C.A.* **30**, 6302 (1936).

## 2-CHLORO-7-METHOXY-5-THIOLACRIDINE

$C_{14}H_{10}ONSCI$

Mol. Wt. 275.74.

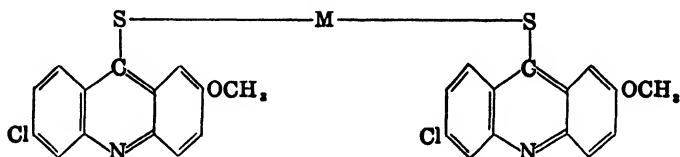


**Use:** Determination of copper and mercury.

2-Chloro-7-methoxy-5-thiolacridine is a red crystalline solid which melts at  $245^{\circ}C$ . It is insoluble in water, but is soluble in both aqueous and alcoholic sodium hydroxide.

**Preparation:** Heat 2 g. of 2,5-dichloro-7-methoxyacridine<sup>1</sup> with 4 g. of potassium xanthate in 6 g. of phenol at  $115^{\circ}C$ . for 3 hours. Cool, pour the mixture into ice-cold water, stir for some time, filter, and wash thoroughly with water. Purify by crystallizing from alcohol.<sup>2</sup>

**Determination of mercury and copper.** 2-Chloro-7-methoxy-5-thiolacridine reacts with mercuric and cupric ions to form insoluble compounds having the following general composition:



in which M represents an atom of copper or mercury. Precipitation is quanti-

tative, and so this reaction can be used for the gravimetric determination of copper and mercury.<sup>3</sup>

**Reagent.** Dissolve 0.11 g. of 2-chloro-7-methoxy-5-thiolacridine in 100-150 ml. of 95 per cent alcohol containing 3.5 ml. of 0.1 N alcoholic sodium hydroxide.

**Procedure.** To determine mercury, treat the substance with fuming nitric acid to convert to a soluble mercuric compound. Make the solution just alkaline with sodium hydroxide or sodium carbonate, and acidify with hydrochloric acid. Avoid an excess of the acid.

To determine copper digest the material with sulfuric acid to convert the copper to copper sulfate, neutralize as above and proceed as follows:

Treat the neutral solution containing 10-20 mg. of mercury or 5-10 mg. of copper in 10 ml. of solution with an excess of the filtered reagent. An excess of the reagent is shown by an orange or reddish color in the supernatant liquid. 100 ml. of the reagent is sufficient for 10 mg. of mercury and 5 mg. of copper. Stir well and allow the mixture to stand for a few hours. Filter through a Gooch crucible, wash with 95 per cent ethyl alcohol until the washings are nearly colorless, and then dry at 100° C. and weigh.

The yellowish-red mercury precipitate contains 26.76 per cent of mercury, and the pinkish-brown copper precipitate contains 9.286 per cent of copper.

The results obtained using this method are within 1 per cent of the theoretical value. Silver and cations of the second and third analytical groups interfere.

The results obtained in the determination of copper and mercury in various salts of these metals are shown in Table 19.

TABLE 19.—DETERMINATION OF COPPER AND MERCURY

Substances	Weight Used g.	Weight of Precipitate g.	Per Cent of Metal (Cu or Hg)	
			Found	Calculated
Mercury .....	0.01128	0.0421	99.88	100
Mercuric oxide .....	0.01505	0.0521	92.40	92.61
Mercuric chloride .....	0.01706	0.0471	73.89	73.85
Mercuric acetate .....	0.02028	0.0489	62.87	62.96
Mercurous chloride .....	0.01665	0.0530	85.19	84.96
Mercuric sulfide .....	0.01305	0.0420	86.14	86.24
Cupric oxide .....	0.00759	0.0653	79.90	79.89
Cupric sulfate .....	0.01542	0.0418	25.17	25.48
Cupric acetate .....	0.01248	0.0428	31.84	31.86
Cupric citrate .....	0.01464	0.0521	33.04	33.47

1. S. J. Das-Gupta, *J. Indian Chem. Soc.* **15**, 160-4 (1938); *C.A.* **32**, 7039 (1938).

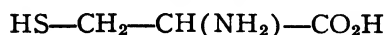
2. S. J. Das-Gupta, *J. Indian Chem. Soc.* **17**, 244-6 (1940).

3. S. J. Das-Gupta, *J. Indian Chem. Soc.* **18**, 43-4 (1941); *C.A.* **36**, 56 (1942).

**CYSTEINE**Synonym:  $\alpha$ -Amino- $\beta$ -thiolactic acid $C_3H_7O_2NS$ 

Mol. Wt. 121.15

Beil. Ref. IV, 506.

**Use:** Detection of copper, iron and manganese.

Determination of cobalt, copper and potassium.

Cysteine is a white crystalline powder which is rapidly oxidized to cystine on exposure to air. It melts at 174-178° C. It is soluble in water, acetic acid, and ammonium hydroxide. The compound is usually obtained in the form of the hydrochloride. It should be stored in tightly closed containers and protected from light.

**Preparation:** Dissolve cystine (for preparation, see page 122) in hydrochloric acid, and reduce by adding pieces of tin foil. At first the tin dissolves without the evolution of hydrogen. As soon as a distinct evolution of hydrogen occurs, dilute the solution, precipitate the tin with hydrogen sulfide, and evaporate the solution to dryness. Dissolve the residue of cysteine hydrochloride in alcohol, and carefully precipitate the cysteine with ammonia. Avoid an excess of ammonia. Filter off the precipitate, wash with alcohol, and dry quickly *in vacuo*.<sup>13</sup> The following method is recommended by Warburg.<sup>2</sup>

**Preparation:** Reduce 50 g. of cystine (for preparation see page 122) with tin and hydrochloric acid according to the method of Friedmann<sup>1</sup> and evaporate the resulting mixture to 70 ml. on a water-bath. Allow to stand for 24 hours at room temperature to obtain crystals of cysteine hydrochloride. Decant the mother liquor and grind the crystals as fine as possible with pure acetone. Filter with suction and repeat the grinding and suction treatment until the acetone is colorless. Dry the product *in vacuo* over sulfuric acid.

**Detection and determination of iron, manganese and copper.** Baumann<sup>3</sup> observed that the oxidation of cysteine to cystine takes place in a neutral, acid or alkaline solution, and that in the presence of iron salts the oxidation is markedly accelerated. Mathews and Walker<sup>4</sup> investigated the influence of pH upon the oxidation of cysteine, and found the oxidation velocity to be a maximum in a nearly neutral solution. They also found that copper accelerates this reaction. Warburg and Sakuma<sup>5,6</sup> have found that cysteine is oxidized only in the presence of heavy metals, and have shown that this oxidation can be used for the detection and determination of heavy metals such as iron, manganese and copper.

Warburg<sup>2</sup> found that pyrophosphate prevents the action of iron and manganese in the oxidation of cysteine, but oxidation due to copper is not affected. Cysteine can therefore be used for the detection and determination of copper in the presence of iron and manganese. This method has been employed for the determination of small quantities of copper in blood, serum and biological liquids.<sup>7-9</sup> The quantity of copper is determined by the rate of absorption of

oxygen by the solution containing copper and to which cysteine and sodium pyrophosphate have been added.

**Determination of cobalt.** Cobalt reacts with cysteine at a pH of 7-8 and in the absence of oxygen to form a cobaltous complex which is usually olive-green in color, but which may be pink in the presence of a large excess of the reagent. The cobaltous complex is rapidly oxidized by air or by ferricyanide to a brown complex which is similar in color to that obtained in the reaction between ammonia and Nessler's reagent. The ratio of cobalt to cysteine in the oxidized complex is 1:3. The cobalt complex has been assigned the formula,  $\text{Co}(\text{SCH}_2\text{—NH}_2\text{—CH—CO}_2)_3\text{H}_2$ .

Nickel at a pH of 7-8 gives a Bordeaux-red complex with cysteine. The color formed by the oxidation of the cobaltous complex with cysteine may be used for the colorimetric determination of cobalt.<sup>10-12</sup>

Nickel, copper, manganese and iron do not interfere unless present in fairly large amounts. A quantity of nickel which is twice that of the cobalt present alters the color of the solution appreciably.

**Procedure.** Place the sample containing not more than 5 mg. of cobalt in a platinum crucible, and add about 1.5 ml. of concentrated sulfuric acid. Place this in a large nickel crucible and evaporate to dryness. Add 75 ml. of a buffer solution having a pH of 7.5, and filter if the solution is not perfectly clear. Then add about 10 mg. of cysteine hydrochloride crystals and mix the solution carefully. Atmospheric oxidation causes the formation of the cobalt complex of the colored compound. Compare the resulting color with that of a standard prepared similarly and simultaneously.

**Determination of potassium.** Potassium may be determined indirectly after precipitating as potassium cobaltinitrite by determining the quantity of cobalt in the precipitate by means of the color obtained in the reaction between cobalt and cysteine.<sup>12</sup> The following procedure is used after precipitating potassium as the cobaltinitrite:

**Procedure.** Dissolve the precipitate in 1 ml. of 1:2 hydrochloric acid and evaporate to dryness. Dissolve the residue in 5 ml. of 12.5 per cent potassium pyrophosphate solution, and add 5 ml. of a solution containing 3.5 mg. of cysteine hydrochloric per ml. Then add 2.5 ml. of 0.1 per cent hydrogen peroxide solution, dilute to 25 ml. (or a suitable volume depending upon the cobalt content) and compare with standards similarly and simultaneously prepared.

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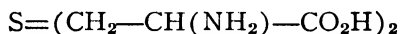
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## CYSTINE

$C_6H_{12}O_4N_2S_2$

Mol. Wt. 204.29

Beil. Ref. IV, 507.



**Use:** Detection of platinum.

Cystine is a white crystalline powder which decomposes without melting on heating. It is slightly soluble in cold water, but is insoluble in alcohol. It is soluble in mineral acids and the alkali hydroxides.

**Preparation:** Wash human hair with a lukewarm soap solution, and then wash two times with cold distilled water and dry. Transfer 2000 g. of the dry, washed hair to a 12-liter pyrex flask and add 4 liters of 20 per cent hydrochloric acid. Fit the flask with an air-cooled reflux condenser, and heat until the biuret test is entirely negative. This usually requires 120 to 148 hours.

Filter the hot mixture, and wash the insoluble residue with distilled water. To the filtrate add 300 ml. of 40 per cent sodium hydroxide solution with stirring, and then cool and add a saturated solution containing 3750 g. of crystallized sodium acetate. Test with Congo red for the presence of free mineral acid. The test should be negative. Care must be taken that the filtrate is not made alkaline with sodium hydroxide. Allow the mixture to stand for 3 days at room temperature, and then filter with suction. Dissolve the solid in 3000 ml. of 3 per cent hydrochloric acid and filter. Treat 2-5 times with decolorizing carbon until the product is completely decolorized. The filtrate should be water-clear or only slightly yellow. Filter immediately to obtain a clear solution.

Precipitate cystine by adding a filtered solution containing 900-1000 g. of crystallized sodium acetate until the Congo red reaction is negative. Allow to stand 5-6 hours, then filter, and wash twice with 100-200 ml. portions of hot distilled water.

Crude sheep's wool that has been freed from grease may be used in place of hair, although the yield is only about one-half as great.<sup>1-4</sup>

**Detection of platinum.** Whitmore and Schneider<sup>5</sup> have studied the use of a cystine as a microchemical reagent for platinum. When a drop of cystine solution is added to a drop of solution containing chloroplatinic acid, and the resulting mixture is allowed to evaporate, poorly formed, pale yellow, tetrahedra appear around the circumference of the drop. Other metals of the platinum group do not yield recognizable crystal forms.

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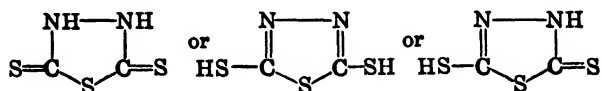
**2,5-DIMERCAPTO-1,3,4-THIODIAZOLE**

Synonym: Mercaptothioketothiodiazole, bismuthol,  
mercaptosulfathiodiazole

 $C_2H_2N_2S_3$ 

Mol. Wt. 150.22

Beil. Ref. XXVII, 677 (600).



**Use:** Detection of antimony, bismuth, copper and lead.

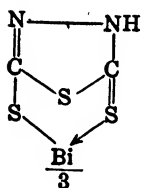
Determination of bismuth.

2,5-Dimercapto-1,3,4-thiodiazole is obtained in the form of needles by crystallizing from ether. It melts at 168° C. with decomposition. It is insoluble in chloroform and benzene, slightly soluble in hot alcohol, and easily soluble in potassium and sodium hydroxide solutions.

**Preparation:** Dissolve 10 g. of hydrazine sulfate in the least possible quantity of water, and to this add 20 g. of carbon disulfide and dilute with alcohol to 3 times the original volume. Place the mixture in a large flask equipped with a reflux condenser and add in small portions a solution of 11 g. of potassium hydroxide in 50 ml. of alcohol. Heat the mixture strongly after each addition. Heat for about 3 hours on a water-bath, and filter from the crystalline mass, which consists largely of potassium sulfate. Immediately decompose the filtrate with concentrated hydrochloric acid. The glistening white needles which separate soon turn yellow on exposure to light. To protect the product from oxidation, filter immediately with suction and dry as quickly as possible on a porous plate and dissolve in ether. Purify the product by distilling off the ether from the mixture. The reagent is obtained as a pure yellow crystalline solid.<sup>1,2,3</sup>

**Detection of bismuth.** A solution of 2,5-dimercapto-1,3,4-thiodiazole in dilute sodium hydroxide reacts with acid solutions of bismuth salts to yield a red precipitate, which is probably a mixture of  $\text{Bi}(\text{C}_2\text{HN}_2\text{S}_3)_3$  and  $\text{Bi}(\text{C}_2\text{HN}_2\text{S}_3)_2\text{Cl}$ . This reaction has been used by Dubsy and Okac,<sup>4-7,9-11,13</sup> as a sensitive test for bismuth.

The reagent reacts as a monobasic acid toward bismuth ions with formation of a red precipitate, and it is possible that in this reaction it is the tautomeric mercaptothioketothiodiazole which causes the formation of the insoluble bismuth salt. This appears due to the formation of a 6-membered ring in which the bismuth atom is united to two unlike sulfur atoms. Apparently the secondary valence bond of the —SH sulfur atom is of significance in the formation of the colored complex, since if the sulfur atom is replaced by oxygen no similar reaction is obtained. In the precipitate which is formed at least one of the bismuth valence bonds is united to an atom of sulfur by means of a secondary valence and 2 to a second atom of sulfur. These 2 atoms of sulfur are in turn each united to carbon atoms which are part of a 5-membered ring<sup>7</sup>



Before carrying out the test with 2,5-dimercapto-1,3,4-thiodiazole, it is necessary to make a previous separation of bismuth from other cations, since the active mercaptothiocarbonyl group reacts with most metals which are precipitated with hydrogen sulfide to give colored precipitates. The reaction may be carried out as a spot test or as a drop reaction. The following procedure is used: <sup>4</sup>

**Reagent.** Dissolve 0.7 g. of 2,5-dimercapto-1,3,4-thiodiazole in 35 ml. of 0.1 N potassium hydroxide. A 1 per cent alcoholic solution may also be used. Both solutions are pale yellow in color.

**Procedure.** Place 1 drop of the solution to be tested, which contains no interfering ions (see below), on a spot plate or in a porcelain dish, and add 1 drop of the reagent. A red or reddish-orange precipitate forms depending upon the concentration of bismuth. By means of this reaction 1.2γ of bismuth may be detected at a concentration of 1:28,000.

A spot test is performed as follows:

**Procedure.** Place 1 drop of a 1 per cent alcoholic solution of 2,5-dimercapto-1,3,4-thiodiazole on a piece of filter paper, and add a drop of the solution to be tested. A red to orange-red spot appears in the center of an almost colorless drop of the reagent. In this way 2γ of bismuth can be detected at a concentration of 1:15,000.

Cadmium, nickel, cobalt, iron manganese, chromium, aluminum, zinc, magnesium, barium, strontium, calcium and the alkalis do not interfere.

Silver, lead, mercury, copper, antimony, tin and ferric iron interfere by the formation of colored compounds with the reagent. Silver reacts with 2,5-dimercapto-1,3,4-thiodiazole to give a yellow compound, but it is possible to detect 3γ of bismuth in the presence of 300γ of silver by means of a spot test. Interference due to silver is eliminated completely by precipitating as silver chloride with hydrochloric acid. Lead, which yields an ochre-colored precipitate with 2,5-dimercapto-1,3,4-thiodiazole, is also precipitated with dilute hydrochloric acid. Mercurous mercury gives a black precipitate with the reagent, but can also be removed by precipitation with hydrochloric acid. Mercuric mercury gives a yellow precipitate and copper a yellowish-brown precipitate. Bismuth can be detected in the presence of copper by converting the copper to a complex ion with potassium cyanide.

**Detection of antimony.** Antimony forms a yellow precipitate with 2,5-dimercapto-1,3,4-thiodiazole. This reaction is very sensitive and can be used

for the detection of 1 $\gamma$  of antimony at a concentration of 1:30,000. If not more than 10 times as much antimony as bismuth is present in the solution to be tested, a yellow central spot due to antimony and an orange ring of the bismuth compound is formed in a spot test. In this way 20 $\gamma$  of bismuth can be detected. Stannous salts yield a yellow compound with 2,5-dimercapto-1,3,4-thiodiazole, and ferric ions and other oxidizing agents lower the sensitivity.

**Detection and determination of copper and lead.** Copper can be detected by means of the brown color or precipitate which forms when 2,5-dimercapto-1,3,4-thiodiazole is added to a solution of a copper salt. As little as 0.02 $\gamma$  of copper can be detected by this reaction. Precipitation is quantitative for low concentrations of copper salts, and so this reaction can also be used for the determination of small quantities of copper. The composition of the copper compound appears to correspond to  $2\text{Cu}\cdot 3$  dimercaptothiodiazole, but it is too variable to permit an accurate determination by weighing in this form. The best practice is to decompose the copper precipitate with nitric acid and determine the copper iodometrically after filtration, concentration, and the addition of bromine. The copper precipitate can be collected in dilutions below 1:1,600,000. Copper can be determined accurately in the presence of iron by first reducing iron to the ferrous state to avoid oxidation of the reagent. It is also possible to determine copper in the presence of zinc, arsenic, antimony, tin, molybdenum and tungsten by using this reaction.

Lead is separated from tin, antimony, molybdenum, bismuth, calcium, strontium and barium by precipitating as the bright yellow compound which forms with 2,5-dimercapto-1,3,4-thiodiazole. The lead is finally determined as lead sulfate.<sup>12,14</sup>

**Determination of bismuth.** Majumdar<sup>15-17</sup> has used 2,5-dimercapto-1,3,4-thiodiazole for the colorimetric determination of small quantities of bismuth. The red precipitate which the reagent yields with solutions of bismuth salts can be peptized by a solution of gum acacia, and the coloration thus obtained used for determining bismuth, since the color intensity follows Beer's law.

**Procedure.** Make the solution to be analyzed slightly acid with nitric acid, and add 5 ml. of 1 N nitric acid and 5 ml. of a 0.5 per cent aqueous solution of gum acacia. Add a little water, and then add dropwise a 0.5 per cent aqueous solution of 2,5-dimercapto-1,3,4-thiodiazole until the color reaches a maximum. Allow to stand a few minutes and compare with standards similarly prepared.

As little as 3 $\gamma$  of bismuth in 20 ml. of solution can be determined in this way.

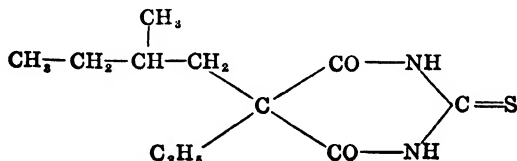
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### ETHYL-(1-METHYLBUTYL)THIOBARBITURIC ACID

$C_{11}H_{18}O_2N_2S$

Mol. Wt. 242.31



**Use:** Detection of copper.

The sodium salt of ethyl-(1-methylbutyl)thiobarbituric acid is a hypnotic, sold under the name of "Pentothal Sodium." It is a light yellow powder which is very soluble in water and moderately soluble in absolute alcohol.

**Preparation:** Add 130 g. of ethyl-(1-methylbutyl)malonic ester to a concentrated solution of sodium ethylate prepared from 34 g. of sodium in absolute alcohol. Add with stirring 60 g. of finely powdered thiourea and reflux for 10 hours. Evaporate the solvent and dissolve the residue in cold water. Precipitate with hydrochloric acid and purify by dissolving in sodium hydroxide and reprecipitating with carbon dioxide. Finally, dissolve the product in cold alcohol, heat to 50° C., and dilute with water to a 50 per cent alcohol content. The free acid precipitates as a white crystalline solid (m.p. 158-9° C.). The sodium salt is formed by treating the product with sodium hydroxide.<sup>1</sup>

**Detection of copper.** Liberalli<sup>2</sup> reports that a 10 per cent solution of the sodium salt of ethyl-(1-methylbutyl)thiobarbituric acid and an equal volume of concentrated ammonium hydroxide gives an intense emerald green color with solutions of copper salts. The color is stable for several hours and seems to be specific for copper. Attempts to use this reaction for the microdetection of copper were unsuccessful.

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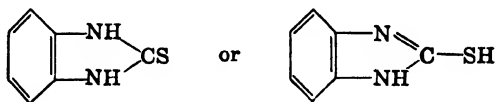
**2-MERCAPTOBENZIMIDAZOLE**

Synonym: *o*-Phenylenethiourea, benzimidazolthione, 2-thiolbenzimidazole

$C_7H_6N_2S$

Mol. Wt. 150.18

Beil. Ref. XXIV, 119.



**Use:** Detection and determination of bismuth, cadmium, copper, gold, lead, mercury, palladium and silver.

2-Mercaptobenzimidazole is a crystalline solid having a bitter taste. It melts at  $292-293^{\circ}C$ . It is only slightly soluble in water but dissolves readily in alcohol.

**Preparation:** Dissolve 1 mole of *o*-phenylenediamine hydrochloride and a little more than 2 moles of ammonium thiocyanate in water and evaporate the mixture on a water-bath to a syrupy consistency. To convert the resulting *o*-phenylenediamine thiocyanate to 2-mercaptobenzimidazole, heat the mass in an air-bath for 1 hour at  $120-130^{\circ}C$ ., and digest the resulting hard mass when cold with cold water. 2-Mercaptobenzimidazole remains behind as a gray-colored solid, while soluble salts pass into solution. Purify the product by dissolving in a little boiling alcohol, and mix the resulting solution with water until a weak turbidity appears. After a time the compound crystallizes as pale violet leaves. Repeated crystallization with animal charcoal yields a colorless product.<sup>1,2</sup>

**Reactions with the metals.** 2-Mercaptobenzimidazole reacts with solutions of various metallic salts to yield insoluble compounds. Copper, cadmium, bismuth, lead, silver, mercury and gold are quantitatively precipitated with this reagent. When an alcoholic solution of 2-mercaptobenzimidazole is added to a solution containing an excess of cupric ions, an amorphous yellow precipitate is obtained, but precipitation is not quantitative. Upon the addition of ammonia, however, precipitation of copper is complete. In the presence of an excess of 2-mercaptobenzimidazole in an alcoholic or a water-alcohol mixture containing ammonia, small quantities of cupric salts form an amorphous green precipitate. The further addition of copper causes a decrease in the quantity of precipitate and an increase in the quantity of copper salts in solution. This imparts to the ethyl alcohol an intense wine-red color. It appears that the amorphous precipitate is an internal complex with 2-mercaptobenzimidazole which dissolves in ethyl alcohol.<sup>3,4</sup>

Kuras<sup>5,6,7</sup> has been able to prepare a number of salts of 2-mercaptobenzimidazole and a few of the heavy metals. The composition of these compounds, and their appearance is given in Table 20:

Bismuth nitrate in an acetic acid solution yields a yellow color when treated with a solution of 2-mercaptobenzimidazole in dilute ethyl alcohol, but upon the subsequent addition of sulfuric or nitric acid, bismuth is quantitatively precipitated as a complex internal salt. In dilute ethyl alcohol containing 2-mercapto-

benzimidazole and ammonia, silver, mercury and gold form amorphous precipitates which become crystalline on warming, and are quantitatively precipitated.<sup>3</sup>

TABLE 20.—SALTS OF 2-MERCAPTOBENZIMIDAZOLE

$\text{Bi}(\text{C}_7\text{H}_5\text{N}_2\text{S})_3 \cdot 3\text{H}_2\text{SO}_4$ .....	Orange-yellow microcrystals
$\text{Bi}(\text{C}_7\text{H}_5\text{N}_2\text{S})_3 \cdot 3\text{HCl}$ .....	Yellow microcrystals
$\text{Bi}(\text{C}_7\text{H}_5\text{N}_2\text{S})_3 \cdot 3\text{HNO}_3$ .....	Pink microcrystals
$\text{Pb}(\text{OH})\text{C}_7\text{H}_5\text{N}_2\text{S}$ .....	Silky white flakes
$\text{Cd}(\text{OH})\text{C}_7\text{H}_5\text{N}_2\text{S} \cdot \text{NH}_3$ .....	Crystalline white powder
$\text{Cu}(\text{OH})\text{C}_7\text{H}_5\text{N}_2\text{S}$ .....	Gray blue powder

Most of the above salts possess the structure of complex internal salts.

**Detection of palladium.** Steigmann<sup>9</sup> reports that 2-mercaptobenzimidazole is an excellent reagent for palladium. Bismuth, mercury, cadmium, copper and cobalt also react, but with suitable precautions the reaction constitutes a satisfactory test for palladium. The blue-black copper precipitate and the blue-green cobalt precipitate are soluble in aqueous sodium hydroxide, and are readily separated from the white precipitates of mercury and cadmium, which are insoluble. The cadmium precipitate is soluble in acetic acid, and can thus be separated from the insoluble mercury precipitate. Bivalent palladium yields with the reagent a yellow-orange precipitate which is insoluble in aqueous sodium hydroxide, while the orange bismuth precipitate is soluble. Thus, palladium gives with 2-mercaptobenzimidazole the only colored precipitate which does not dissolve in sodium hydroxide. The test is carried out as follows:

**Procedure.** Place a drop of a hot saturated solution of the sodium salt of 2-mercaptobenzimidazole on a piece of filter paper and add a drop of the solution to be tested. A yellow-orange spot or ring, which is stable toward 2 per cent sodium hydroxide, indicates the presence of palladium. This test detects 0.25 $\gamma$  of palladium at a concentration of 1:200,000.

**Determination of copper, lead and cadmium.** The reaction of 2-mercaptobenzimidazole with copper may be used for the quantitative determination of the latter:<sup>8</sup>

**Procedure.** To a neutral aqueous solution containing 0.1 g. of cupric sulfate, or its equivalent, add 10-15 ml. of a 1 per cent solution of 2-mercaptobenzimidazole in 50 per cent alcohol. Then add a few drops of concentrated ammonium hydroxide, and heat on a water-bath until the precipitate collects in a loose mass. The odor of ammonia disappears and the solution becomes colorless. Filter while hot, wash with hot water and ignite in a crucible and weigh as  $\text{CuO}$ .

By using the procedure described above, lead is precipitated as a basic salt,  $\text{Pb}(\text{OH})\text{C}_7\text{H}_5\text{N}_2\text{S}$ , and cadmium as an addition compound  $\text{Cd}(\text{OH})(\text{C}_7\text{H}_5\text{N}_2\text{S}) \cdot \text{NH}_3$ . Both of these salts form large crystals, which can be collected on a Gooch filter, dried, and weighed. The maximum errors obtained in these

determinations are: lead,  $\pm 0.18$  per cent; copper,  $\pm 0.25$  per cent; and cadmium,  $\pm 0.11$  per cent.

The presence of alkali metals and alkaline earths in the aqueous solution does not appear to interfere with the precipitation, or otherwise affect the results.<sup>8</sup>

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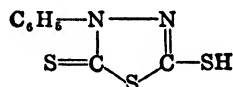
## MERCAPTOPHENYLTHIOTHIAZOLONE

Synonym: 5-Mercapto-3-phenyl-2-thio-1,3,4-thiadiazolone-2, phenyldithiadiazoloneethiol, Bismuthiol II

$C_8H_6N_2S_3$

Mol. Wt. 226.31

Beil. Ref., XVII, 678.



**Use:** Detection of antimony, bismuth, copper, lead, mercury, nickel and silver.

Determination of bismuth.

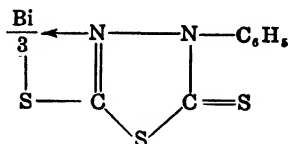
This compound consists of fine white needles which melt at  $250^\circ C$ . It is soluble in water and hot alcohol.

**Preparation:** Dilute 9.8 ml. of phenylhydrazine with 53 ml. of alcohol and mix with 19 ml. of carbon disulfide in the cold. Form the potassium salt of the reagent by heating the crystalline mass for 10 hours on a water-bath under reflux with a solution of 12 g. of potassium hydroxide in 76 ml. of absolute alcohol. Filter while hot and cool. The raw product, which crystallizes from the filtrate on cooling, is separated by filtration. Recrystallize twice from hot alcohol. The free acid may be formed by acidifying the potassium salt with hydrochloric acid.<sup>1</sup>

**Detection of bismuth and other metals.** An aqueous or alcoholic solution of mercaptophenylthiothiazolone or its potassium salt reacts with trivalent bismuth in aqueous solution to form an orange-red or brownish-red precipitate. The formation of the bismuth compound may be caused by the replacement of the hydrogen atom of the mercapto group by the metal, and coordination



of the metal atom with the adjacent nitrogen atom. The formula for this compound formed in this way is



This reaction is characteristic but not specific, since colored precipitates are also obtained with silver, lead, mercury, copper, cadmium, nickel, iron, tin and antimony ions. This reaction has been used by Dubsy and Trtilek<sup>2-4,6-9</sup> for the detection of bismuth.

**Reagent.** Dissolve 1.3 g. of the potassium salt of the reagent ( $C_8H_5N_2S_3K$ ) in 50 ml. of cold water.

**Procedure.** Add 1 drop of the reagent to a drop of the solution to be tested. A reddish-colored precipitate forms if bismuth is present. The sensitivity of this reaction is 0.0012 mg. of bismuth at a dilution of 1:28,000.

Majumdar,<sup>10</sup> however, states that the color reaction is perceptible at a dilution of 1:6,000,000 if a nitric acid solution is used instead of a chloride solution.

Only 1 drop of an aqueous solution of the reagent is used in making the test to avoid the separation of free mercaptophenylthiothiodiazolone, which might occur with greater concentration of the potassium salt, since the bismuth salts are normally present in acid solutions. The free reagent is white, but it oxidizes in the presence of air to a yellow disulfide. The color of this compound is different from that of the characteristic bismuth salt, but some confusion might result with low concentrations of bismuth. In any event the presence of the free reagent lowers the sensitiveness of the bismuth test.

The reagent also forms colored precipitates with a number of other metals. It gives yellow precipitates with gold, mercury, lead, silver, platinum, arsenic and antimony; white with cadmium and zinc; brown with copper; brick-red with tin; and red with palladium.<sup>3,10</sup>

The bismuth salt of mercaptophenylthiothiodiazolone is prepared by dissolving 1.05 g. of bismuth chloride in water with the aid of 2 N hydrochloric acid, and warming with a solution containing 2.6 g. of reagent. The composition of this compound appears to be  $Bi(C_8H_5N_2S_3)_3 \cdot 2H_2O$ . When an alcoholic solution of bismuth chloride is added to an alcoholic solution of the reagent, the orange precipitate which first forms gradually changes to red, and this on warming changes to a yellow modification. The red product once again appears on cooling. The red compound has the formula,  $Bi(C_8H_5N_2S_3)_2Cl$ .

When a warm solution of copper acetate is treated with mercaptophenylthiothiodiazolone, a yellow ochre-colored copper salt of the following composition is formed,  $2[Cu^+(C_8H_5N_2S_3)] \cdot C_8H_5N_2S_3$ . The brownish-yellow dihydrate is formed when the reaction is carried out in a cold solution.

**Determination of bismuth.** The reaction of bismuth salts with mercaptophenylthiothiodiazolone may be used for the gravimetric and colorimetric estimation of bismuth. The air-dried bismuth compound loses only 2.94 per cent of water when heated for several hours at 105° C., and there is no further loss of water on heating to 130° C. The composition of the compound obtained by heating to 105° C. corresponds to the formula  $\text{Bi}(\text{C}_8\text{H}_5\text{N}_2\text{S}_3)_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ .

**Procedure.** To a solution of bismuth nitrate, which should contain about 10 ml. of 1 N nitric acid per 100 ml., add slowly with stirring a few ml. of a 1 per cent aqueous solution of the potassium salt of the reagent until precipitation is complete. Heat with stirring until the precipitate coagulates and the supernatant liquid becomes clear. Filter quickly through a Gooch crucible, wash with hot water, dry at 100° C., and weigh. The factor for bismuth is 0.2340.

Results claimed by this method are excellent, although many of the heavy metals interfere.<sup>10</sup>

Majumdar<sup>5,10</sup> reports that as little as 3γ of bismuth in 20 ml. of solution can be estimated colorimetrically by the red color which is formed in the reaction with mercaptophenylthiothiodiazolone. The color system obeys Beer's law over a wide range of bismuth concentration. If the quantity of bismuth exceeds  $3.5 \times 10^{-4}$  g., a solution of gum acacia must be used to stabilize the colloidal suspension of the red compound. Full development of the maximum color intensity occurs within 1-2 minutes.

**Procedure.** Transfer to the tube of a Duboscq colorimeter a few ml. of bismuth nitrate solution containing sufficient nitric acid to keep the bismuth in solution. Then add 1 ml. of a 0.5 per cent aqueous solution of gum acacia, a few ml. of water, and then add dropwise with shaking a 0.5 per cent aqueous solution of the potassium salt of the reagent until the maximum color has developed. Dilute to 20 ml., mix thoroughly, and compare with a suitable standard similarly prepared. If a spectrophotometer is used, measure the transmittance at 460 mμ.

If the bismuth solution contains ions other than nitrate, add 5 ml. of 1 N nitric acid in addition to 5 ml. of the gum acacia solution.

For the determination of 1 mg. of bismuth or more, transfer the bismuth solution to a 100-ml. volumetric flask, add a few ml. of the 0.5 per cent gum acacia solution, dilute with water almost to the mark, and then add a few ml. of the reagent solution until there is no further increase in the color. Dilute to the mark and mix thoroughly. Transfer 20 ml. of this solution to a colorimeter and compare with a standard. Add the same quantities of nitric acid, reagent, and gum acacia to both the unknown and standard.

Interfering ions, and permissible quantities of various substances, are given in Table 21. These values were determined by using the above procedure with 0.26 mg. of bismuth, 5 ml. 1 N nitric acid, and 5 ml. of gum acacia solution.

TABLE 21.—INTERFERENCE WITH BISMUTH DETERMINATION

Ion	Amount Permissible mg.	Cause of Interference
Cupric .....	0.07	Color of ion
Cobalt .....	2	Color of ion
Nickel .....	9	Color of ion
Zinc .....	10	Precipitate
Cadmium .....	0.5	Precipitate
Lead .....	1	Precipitate
Mercuric .....	0.5	Precipitate
Silver .....	0.3	Precipitate
Chloride .....	50	Precipitate
Arsenic (III) .....	0.05	Precipitate
Antimony .....	0.1	Precipitate
Stannous .....	0.2	Precipitate

The following ions do not interfere in concentrations below the following: Manganese, 100 mg.; ferrous, 100 mg.; nitrate, 100 mg.; nitric acid, 1 ml. ( $d = 1.4$ ); sulfate, 100 mg.; oxalate, 100 mg.; tartrate, 100 mg.; sulfurous acid (saturated solution), 10 ml.

Results obtained using this method are shown in Table 22.

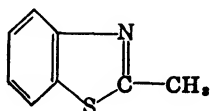
TABLE 22.—DETERMINATION OF BISMUTH

Bismuth Taken mg.	Bismuth Found mg.	Error mg.
6.48	6.46	-0.02
3.888	3.920	+0.032
2.592	2.580	-0.012
1.296	1.30	+0.004
0.518	0.524	+0.006
0.259	0.256	-0.003
0.1037	0.1037	0.000
0.065	0.066	+0.001
0.0065	0.0065	0.000
0.0039	0.0040	+0.0001

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**2-METHYLBENZOTHAIAZOLE** $C_8H_7NS$ 

Mol. Wt. 149.20    Biol. Ref. XXVII, 46(214).

**Use:** Detection of antimony and bismuth.

2-Methylbenzothiazole is an oily liquid having an odor like that of pyridine. It is soluble in alcohol and hydrochloric acid.

**Preparation:** Mix 12.6 g. of zinc *o*-aminothiophenolate, 9 ml. of acetic anhydride and 25 ml. of glacial acetic acid, and heat for 2 hours in a flask equipped with a reflux condenser. Allow to cool, and let stand for several hours. Separate by decantation the liquid from the solid zinc acetate, and then distill. Retain the liquid boiling at 230-235° C.<sup>1,2</sup>

**Detection of bismuth and antimony.** 2-Methylbenzothiazole, like many organic nitrogenous compounds, reacts with bismuth and potassium iodide to give a red or orange-red precipitate ( $C_8H_7NS \cdot KBiI_4$ ); and with antimony to give a yellow precipitate.<sup>3</sup>

The test is performed by adding 1 ml. of molar potassium iodide to the solution to be tested, which is 3 molar in nitric acid, and then adding 1 ml. of a 1 per cent alcoholic solution of 2-methylbenzothiazole. The results are given in Table 23, which is taken from the work of Naiman.<sup>3</sup>

TABLE 23.

5 ml. of Bi. Solution mg./ml.	Immediate Reaction		
	Color Reaction	Turbidity	Crystals
0.050	Red-orange	Marked	Red needles—15 min.
0.025	Red-orange	Moderate	Red needles—2 hours
0.020	Red-orange	Slight	Red needles—2 hours
0.0125	Red-orange	Faint	Red microcrystals—4 hours
0.010	Negative	Negative	Red microcrystals—24 hours

With antimony a yellow turbidity or yellow crystalline solid appears. The sensitivity of the antimony reaction is about the same as that with bismuth.

A drop reaction for bismuth or antimony is carried out as follows:

**Procedure.** Place 1 drop of solution to be tested, which is 3 molar in nitric acid, on a spot plate, and mix with 1 drop of molar potassium iodide and 1 drop of a 1 per cent alcoholic solution of 2-methylbenzothiazole. An immediate

red turbidity appears with bismuth solutions containing only 0.05 mg. of bismuth per ml.

West and Tokos<sup>4</sup> report that with proper precaution as little as 0.3 $\gamma$  of bismuth can be detected at a limiting concentration of 1:40,000.

The precipitate formed by bismuth and 2-methylbenzothiazole may, because of its color, be observed even in the presence of considerable quantities of antimony, although the test is not reliable if the quantity of antimony present is greater than ten times the amount of bismuth. Silver, lead and mercurous ions form precipitates with potassium iodide, which is used in the test, and may therefore interfere with the detection of bismuth. This interference is, however, easily eliminated by the following treatment: add sufficient molar potassium iodide to precipitate completely these ions and form a yellow supernatant solution of  $\text{BiI}_4^-$  ions, and then filter off the precipitate before applying the bismuth test. Copper, ferric iron, and other oxidizing agents may interfere with the test by oxidizing the iodide ion to free iodine, but this interference is avoided by adding a few drops of a 5 per cent solution of sodium bisulfite until the brown color of the iodine just disappears. Mercuric ions do not interfere if a sufficient excess of potassium iodide solution is added to dissolve the precipitate of mercuric iodide. Mercuric ions form a white crystalline precipitate with 2-methylbenzothiazole, but this does not prevent the observation of the red color of the bismuth compound. Large quantities of iodide, cyanide, bisulfite and thiosulfate dissolve the bismuth precipitate and inhibit the test. The test is also inhibited by nitric and hydrochloric acids more concentrated than 3 M, and by concentrated ammonium hydroxide.

West and Tokos<sup>4</sup> have studied the effect of various ions on the bismuth test with 2-methylbenzothiazole, and have summarized their results as follows:

(a) *Positive interference*:  $\text{Ti}^+$ ,  $\text{Pb}^{+2}$ ,  $\text{Sb}^{+2}$ ,  $\text{Sb}^{+5}$ .

(b) *Negative interference*:  $\text{Sr}^{+2}$ ,  $\text{Ba}^{+2}$ ,  $\text{NO}_2^-$ ,  $\text{HPO}_4^{-2}$ ,  $\text{CN}^-$ , tartrate, citrate.

(c) *Masking interference*:  $\text{Cu}^{+2}$  (brown),  $\text{Au}^{+3}$  (brown),  $\text{Hg}^+$  (black),  $\text{Hg}^{+2}$  (brown),  $\text{Cr}^{+3}$  (green),  $\text{Cr}_2\text{O}_7^{-2}$  (green),  $\text{TeO}_3^{-2}$  (black),  $\text{Fe}^{+2}$  (brown),  $\text{Fe}^{+3}$  (brown),  $\text{Pd}^{+2}$  (brown), and colored ions, such as  $\text{UO}_2^{+2}$ ,  $\text{UO}_4^{-2}$   $\text{Ru}^{+3}$ , and  $\text{Rh}^{+3}$ .

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## OXANILIC ACID THIOAMIDE

$\text{C}_8\text{H}_8\text{ON}_2\text{S}$

Mol. Wt. 180.20

Beil. Ref. XII, 288.



**Use:** Determination of cobalt, copper and nickel.

This reagent is obtained as yellowish crystals from alcohol. It melts at 176° C. It is readily soluble in acetone, and acetic acid, but is only moderately soluble in alcohol, benzene, ether and chloroform.

**Preparation.** *Phenyloxamide*: Mix 10 g. of oxamide with 60 g. of aniline and heat to boiling for 15 hours in an open vessel. Filter hot, acidify the filtrate with dilute hydrochloric acid, and again filter. Wash the residue with alcohol and dry.<sup>1</sup>

*Oxanilic acid thioamide*: Place 50 g. of phenyloxamide and 500 g. of xylene in a flask fitted with a reflux condenser, and heat to boiling in an oil bath. To the boiling liquid, add 27 g. of finely powdered phosphorous pentasulfide and heat for 30 minutes with frequent rotation. Filter hot from impurities, wash the residue with xylene, and allow the filtrate to cool. The reagent crystallizes almost completely as brown-yellow needles.<sup>2</sup>

**Reactions.** Oxanilic acid thioamide reacts as a weak acid, since it exists in equilibrium with a tautomeric enol form.



The hydrogen atoms of the enolic OH and SH groups are replaceable by metal ions under favorable conditions. This reagent yields characteristic colored precipitates with most metals of the sulfide groups, although some of these salts are unstable and decompose into sulfides. Precipitation of copper, cobalt and nickel is quantitative, but the precipitates so obtained retain the excess reagent so tenaciously that they cannot be dried and weighed. It is best to precipitate these metals with oxanilic acid thioamide, and then to determine the copper iodometrically, cobalt as the sulfate, and nickel as the oxide.

**Determination of copper.** Copper is determined as follows:

**Procedure.** If the solution to be analyzed is acidic, add ammonia cautiously until the mixture is barely acidic and then dilute to 150 ml. Add 2 g. of sodium acetate, and add dropwise a 1 per cent solution of the reagent until precipitation is complete. Filter, wash the violet precipitate with water and alcohol, ignite to cupric oxide, and determine the copper iodometrically.<sup>3</sup>

**Determination of cobalt.** Use the following procedure for determining cobalt:

**Procedure.** Precipitate cobalt from an aqueous solution by the addition of the sodium salt of oxanilic acid thioamide. After the dark brown precipitate has formed, add a little 2 N hydrochloric acid to coagulate it, filter, wash the residue with hot water, ignite, and convert to cobalt sulfate for the final determination.<sup>3</sup>

**Determination of nickel.** The procedure for the determination of nickel is the same as that for copper except that the precipitation is made from a slightly ammoniacal solution. After filtration, the precipitate is washed with water and ethyl alcohol and ignited to nickel oxide.

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### PHENYLHYDRAZINEPHENYLTHIOCARBAZINATE

$C_{13}H_{16}N_4S_2$

Mol. Wt. 292.38



**Use:** Detection of mercury.

The reagent is a white crystalline solid.

**Preparation:** Add a little phenylhydrazine to a solution of carbon disulfide in benzene. Collect the white crystalline solid which forms, and purify by recrystallizing from alcohol. \*

**Detection of mercury.** A bright reddish-purple precipitate forms immediately when a few drops of a 10 per cent solution of the reagent in acetone is added to a dilute solution of mercury nitrate. This reaction is sensitive to about 10 parts per million of mercury. Many other metals yield colored precipitates with the carbazinate, but only mercury yields a bright reddish-purple precipitate. Only a very small quantity of the reagent should be used, since a large excess may result in the formation of colored precipitates with other metals. Chromate, molybdate and vanadate must be absent.<sup>1,2</sup>

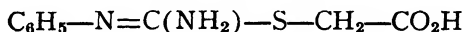
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### PHENYLTHIOHYDANTOIC ACID

$C_9H_{10}O_2N_2S$

Mol. Wt. 210.25

Beil. Ref. XII, 411.



**Use:** Detection of antimony, bismuth, cobalt, copper and mercury.

Determination of antimony, bismuth, cadmium, cobalt, copper, lead and silver. Phenylthiohydantoic acid is a white to yellowish crystalline powder. It melts at 157-158° C. It is sparingly soluble in cold water, but is soluble in hot water. It is only slightly soluble in alcohol, ether and benzene. It is moderately soluble in acids and alkalis.

**Preparation:** Mix 189 g. of monochloroacetic acid and 152 g. of ammonium thiocyanate in a round-bottom flask, and add 186 g. of aniline and 930 ml. of methyl alcohol or ethyl alcohol. Heat the mixture under reflux on a water bath for several hours, and allow the mixture to stand until the undissolved material has settled. Pour the clear brownish liquid into a large evaporating dish and allow to cool. Stir if necessary to hasten crystallization. Filter the yellow crystals on a Buchner funnel, wash with water, and dry. Purify by recrystallizing from alcohol and then from water.<sup>1</sup>

**Detection of cobalt.** Pozzi-Escot<sup>2</sup> first suggested the use of phenylthiohydantoic acid as a qualitative reagent for cobalt. The reagent reacts with cobalt salts in an ammoniacal solution to yield a purple-red precipitate. Nickel yields a brown color with the reagent. Gutzeit<sup>8</sup> has also used this compound as a reagent for nickel.

**Determination of cobalt.** Willard and Hall<sup>4-6</sup> have studied the reaction of phenylthiohydantoic acid with solutions of cobalt salts, and report that precipitation is quantitative in a slightly ammoniacal solution. The precipitate is usually brownish or purplish-red in color. Its composition varies somewhat so that it cannot be weighed, but by converting the cobalt to a weighable form this reaction may be used for the determination of the metal. The reaction is also useful for the separation of cobalt from arsenic, uranium, vanadium, titanium, tungsten, molybdenum, zinc, manganese, chromium, aluminum, magnesium and calcium. Ferric iron in the presence of ammonium citrate usually contaminates the cobalt precipitate slightly. Nickel is always precipitated with cobalt, although the nickel precipitate dissolves in concentrated ammonium hydroxide. The following procedure is used for the separation of cobalt from many metals including iron.

**Procedure.** To a solution containing about 25 mg. of cobalt and not more than 1.0 g. of iron, add 8 g. of citric acid and neutralize with concentrated ammonium hydroxide, and then add 5 ml. in excess. Heat to 35° C. and add 0.7-1.0 g. of phenylthiohydantoic acid dissolved in 30 ml. of alcohol. The total volume of the solution should be about 300 ml. Stopper the flask and shake for several minutes. Heat to boiling and filter, and wash the residue with 0.5 per cent ammonium citrate until the washings give no test for iron. Proceed with the determination of cobalt by one of the usual methods, such as igniting to the oxide or sulfate or by electrolysis. The oxide obtained by ignition of the precipitate to  $\text{Co}_3\text{O}_4$  is contaminated with a little sulfate. Fairly good results are obtained if the oxide is empirically assumed to be  $\text{Co}_2\text{O}_3$ . Ignition to cobalt sulfate at 550° C. gives high results. Results obtained by the electrolytic method are very satisfactory.

To determine the cobalt as sulfate, dissolve the oxide in nitric acid, evaporate to dryness with sulfuric acid, and ignite at 550° C. The results obtained in a number of analyses in which 1 g. of iron was present are shown in Table 24.

Cuvelier<sup>7</sup> has used phenylthiohydantoic acid for the separation of cobalt from nickel or zinc.

Isibasi<sup>8</sup> has studied the proper heating temperature for the cobalt salt of phenylthiohydantoic acid and recommends an ignition temperature of 1050° C. for the determination of the cobalt as the oxide.

Willard and Hall<sup>6</sup> have proposed a titrimetric method for the determination of cobalt after first separating from interfering substances by means of phenylthiohydantoic acid. The following method is described for the determination of cobalt in alloy steels:

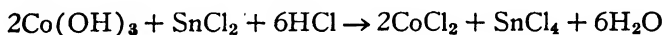


TABLE 24.—DETERMINATION OF COBALT WITH PHENYLTHIOHYDANTOIC ACID

(In the presence of 1.0 g. of iron)

Cobalt Used g.	Cobalt Found g.	Error mg.
0.0320	0.0319	—0.1
0.0245	0.0250	+0.5
0.0238	0.0241	+0.3
0.0270	0.0265	—0.5
0.0306	0.0303	—0.3
0.0337	0.0339	+0.2

**Procedure.** Treat 0.7 g. of the sample to be analyzed with 40 ml. of 1:1 hydrochloric acid, and add slowly 1-2 ml. of 85 per cent phosphoric acid and 3 ml. of nitric acid, and then keep the mixture hot until solution is complete. Add 7 g. of citric acid, neutralize with ammonium hydroxide, and add 6 ml. in excess. Add to the hot solution with stirring 1 g. of phenylthiohydantoic acid dissolved in 30 ml. of hot water. Boil for a few minutes with stirring, filter, dry and ignite. Fuse the ignited residue with potassium pyrosulfate and dissolve in water. Oxidize to the trivalent state by the perborate method of Engle and Gustavson,<sup>9</sup> which is carried out as follows: In a volume of 100 ml. acidify with dilute sulfuric acid and add 5 ml. in excess, and then add 1-2 g. of dry sodium perborate. Make the mixture strongly alkaline with sodium hydroxide and boil for 10 minutes to decompose the excess perborate. Now reduce the trivalent cobalt with an excess of standard stannous chloride solution in an atmosphere of carbon dioxide, and titrate the excess with a standard dichromate solution. The stannous chloride solution is prepared so that each 30 ml. contains 15 ml. of concentrated hydrochloric acid. The reaction between stannous chloride and cobalt is given by the following equation:



The reduction must be carried out in an atmosphere of carbon dioxide. After the reduction, add an excess of standard potassium dichromate solution, discontinue the addition of carbon dioxide, and transfer the mixture to a beaker. Add 30 ml. of 5 N ferric chloride to increase the delicacy of the end-point, and titrate the excess dichromate with standard ferrous sulfate solution. Use potassium ferricyanide as an external indicator. One ml. of 0.05 N stannous chloride solution = 0.29405 mg. of cobalt.

Results obtained using this method are shown in Table 25.

As much as 1 g. of iron does not interfere with this determination.

**Determination of copper.** Copper, lead, mercury, cadmium, bismuth, and antimony in acetic acid solutions are precipitated quantitatively with phenylthiohydantoic acid. Tin and arsenic, however, are not precipitated. The antimony and the bismuth compounds are soluble in alcohol. The copper precipitate

is bright yellow in color, but it decomposes with the formation of enough sulfide to give the precipitate a dirty yellow color. The following method is used for the separation and the determination of copper: <sup>10</sup>

TABLE 25.—DETERMINATION OF COBALT

Co Used g.	0.05 N SnCl <sub>2</sub> Used ml.	0.05NK <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> Used ml.	Co Found g.	Error g.
0.0352	28.80	16.85	0.0352	0.0
0.0252	28.65	20.08	0.0252	0.0
0.0227	28.65	20.98	0.0226	-0.1
0.0318	28.98	18.21	0.0317	-0.1

**Procedure.** Neutralize the solution with ammonia and add 5 ml. of glacial acetic acid. If metals which are precipitated by ammonium hydroxide are present, add 7 g. of citric acid for each 1 g. of the metal. Dilute to 300-400 ml., add 0.5 g. of phenylthiohydantoic acid dissolved in water, and then add dilute ammonium hydroxide until a precipitate begins to form. Boil for a few minutes and if the solution is not colorless, add a little more ammonium hydroxide. Avoid an excess as this causes a partial solution of the precipitate. Filter hot and wash the precipitate with hot water. Ignite the precipitate, fuse the oxide with potassium pyrosulfate, dissolve in water, and determine the copper by any of the standard methods.

**Detection and determination of antimony, lead, silver, mercury, copper cadmium and bismuth.** Several metals, including lead, silver, cadmium, copper, cobalt and antimony, are precipitated quantitatively by means of phenylthiohydantoic acid.<sup>11,12</sup> The use of phenylthiohydantoic acid for the determination of most of these metals appears to offer little advantage over other and better known methods. Lasseur,<sup>11</sup> however, has proposed the following method for the separation and determination of antimony.

**Procedure.** To 150 ml. of the solution to be tested, containing not more than 0.065 g. of antimony, add 5 ml. of 1 N acetic acid and 0.5 g. solid phenylthiohydantoic acid. Heat to boiling and boil for 5-6 minutes. Filter through a Gooch crucible and wash the residue with a little water. Place the precipitate and asbestos in a beaker and treat with 20 ml. of hot alcohol. Add 1 ml. of glacial acetic acid and a little sodium sulfide solution. Filter off the precipitate of antimony sulfide and dissolve this precipitate by pouring four 20-ml. portions of hot sodium sulfide solution through the filter, and finally wash with 60 ml. of water. Add 5 g. of potassium cyanide and electrolyze the mixture at 70° C.

Phenylthiohydantoic acid gives a non-specific but delicate precipitate with mercury. Similar yellow precipitates are obtained with copper, bismuth and antimony in 5 per cent acetic acid. The reaction with mercury is sensitive to 5 p.p.m.<sup>13,14</sup>

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### PHENYLTHIOSEMICARBAZIDE

$C_7H_9N_3S$

Mol. Wt. 167.20

Beil. Ref. XV, 294.



**Use:** Detection of cobalt, copper, nickel and platinum.

Determination of ruthenium.

This compound is a crystalline solid melting at 200-201° C. with some decomposition. It is slightly soluble in water, ether, chloroform and benzene, and is readily soluble in hot alcohol.

**Reaction with metals.** Phenylthiosemicarbazide reacts with a number of metals to give color reactions which may be used for their detection.<sup>1,2,3</sup> These reactions are shown in Table 26.

TABLE 26.

Metal	Reaction	Minimum Amount Detectable
Nickel in NaOH solution	Dark green color	$9.8 \times 10^{-6}$
Cobalt in NaOH solution	Green color	$9.8 \times 10^{-7}$
Cobalt in $NH_4OH$ solution	Green precipitate	
Copper in HCl or acetic acid	Deep blue color	$3.2 \times 10^{-7}$
Platinum in $Na_2CO_3$ solution	Deep green color	$2 \times 10^{-6}$

**Preparation:** Mix equal molecular quantities of phenylhydrazine hydrochloride and ammonium thiocyanate with 2.5 times as much absolute alcohol, and boil for 12 hours on a water bath under reflux. Allow to cool, and let stand 12 hours. Filter off the crystalline precipitate, and wash out the ammonium chloride with cold water. Recrystallize the residue 1-2 times from alcohol.<sup>5</sup>

**Determination of ruthenium.** Phenylthiosemicarbazide reacts with ruthenium in a hot acid solution to give a red to red-violet color. The color intensity is much greater in 4 N hydrochloric acid than in a 1 N acid solution. The sensitivity is said to be greater than that of the thiourea reaction.<sup>4</sup>

The colored compound can be extracted with butyl alcohol from the diluted acid solution, and the color can be observed with 0.5γ of ruthenium in 0.5 ml. of the alcohol. Ferric iron interferes by causing a turbidity or a red color, but this is not important practically, since ruthenium is usually isolated as the tetroxide before the final determination.

**Procedure.** Adjust the acidity of the sample to 4 N in hydrochloric acid, and to 10 ml. of this solution, containing up to 25γ of ruthenium, add 0.5 ml. of a freshly prepared 1 per cent alcoholic solution of phenylthiosemicarbazide. Heat in a boiling water bath for 10 minutes, cool to room temperature, and dilute with water to 25 ml., or to a smaller volume. Determine the transmittancy of the solution at once, using a blue or green filter.

1. F. Feigl, *Oesterr. Chem.-Ztg.* **26**, 85 (1923).
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3. T. Naito and M. Suzuki, *J. Pharm. Soc. Japan.* **56**, 807-11 (1936); *C.A.* **33**, 71 (1939).
4. E. B. Sandell, *Colorimetric Determination of Traces of Metals*, p. 389, Interscience, New York (1944).
5. E. Fischer and E. Besthorn, *Ann.* **212**, 325 (1882).

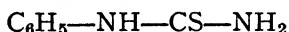
## PHENYLTHIOUREA

Synonym: Phenylthiocarbamide

$C_7H_8N_2S$

Mol. Wt. 152.21

Beil. Ref. XII, 388.



**Use:** Detection of copper, gold, mercury, palladium, platinum and silver.

Phenylthiourea consists of white bitter needles. It melts at 154° C., and has a sp. gr. of 1.3. It is soluble in 400 parts of cold water and 17 parts of boiling water. It is soluble in alcohol.

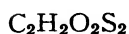
**Preparation:** Heat aqueous solutions of molecular quantities of aniline hydrochloride and ammonium thiocyanate for several hours on a boiling water bath, and then evaporate to dryness. Heat the residue for 2-3 hours at 100° C. Extract ammonium chloride from the residue with cold water, and recrystallize the undissolved portion from boiling alcohol.<sup>1,2</sup>

**Reaction with mercury, copper, silver and metals of platinum group.** The addition of 5 drops of a 2 per cent alcoholic solution of phenylthiourea to 1 ml. of a solution containing mercurous ions gives a grayish turbidity, and a grayish-black precipitate. The limit of sensitivity is 20γ per ml. A similar reaction with silver salts gives a yellow solution, and yellowish-brown precipitate (limit of sensitivity 10γ). With cuprous salts a white turbidity and a white precipitate is obtained (limit of sensitivity is 10γ). Auric, platinum, and palladous ions give a yellow turbidity and a yellow precipitate. Mercuric ions react only in concentrations of at least 1000γ per ml. with a formation of a white tur-

bidity. Acids, alkalies, and salts of the following ions do not interfere: ferrous, ferric, aluminum, bismuth, manganese, zinc, cadmium, nickel, cobalt, antimony, pentavalent arsenic, stannous, thallium, ceric, tungsten, molybdenum, vanadium, zirconium, selenium, tellurium, lanthanum, tantalum, columbium, erbium, ytterbium, barium, calcium, strontium, beryllium, potassium, sodium, lithium and cesium.<sup>3</sup>

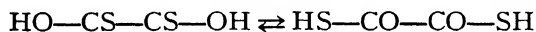
1. H. Salkowski, *Ber.* **24**, 2728 (1891).
2. P. de Clermont, *Bull. soc. chim.* [2] **25**, 242 (1875).
3. M. Ya. Shapiro and M. I. Rud'. *J. Applied Chem. (U.S.S.R.)*, **11**, 140-1 (1938); *C.A.* **32**, 4459 (1938).

## POTASSIUM DITHIOOXALATE



Mol. Wt. 122.16

Beil. Ref. II, 565(244).



**Use:** Detection and determination of cobalt, iron and nickel.

Free dithiooxalic acid is known only in aqueous solutions. The potassium salt is obtained as colorless prisms from water. This compound dissolves in water to form a yellow colored solution.

TABLE 27

Salt	Reaction
Silver nitrate	Orange precipitate which rapidly turns black
Lead acetate	Orange precipitate which rapidly turns black
Mercurous nitrate	Black precipitate
Mercuric chloride	Pale yellow precipitate which is stable on boiling
Bismuth nitrate	Light yellow precipitate which turns dark brown on boiling
Cadmium chloride	Pale yellow precipitate
Copper sulfate	Dark brown precipitate which is soluble in an excess of the reagent with a green solution. This turns black on boiling
Antimony chloride	Yellow precipitate which turns brick red
Stannic chloride	Light yellow color
Stannous chloride	Reddish-brown color
Ferrous sulfate	Brownish-pink color
Ferric chloride	Brownish-pink color
Zinc sulfate	Pale yellow color
Nickel sulfate	Magenta color which is stable on boiling (this is the most characteristic color given by the metals)
Cobalt nitrate	Deep reddish brown color
Manganous sulfate	Yellow color
Palladium chloride	Deep brown color
Platinous chloride	Reddish brown color
Platinic chloride + sodium carbonate	Reddish brown color

**Preparation:** Add one mole of oxalyl chloride in small quantities and at room temperature to two moles of ethyl thioalcohol. After all action has ceased,

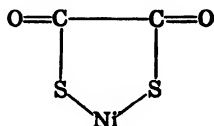
heat gently to remove hydrogen chloride and the excess of either reagent. Dissolve the resulting ethyl dithiooxalate in ethyl alcohol and add an equivalent quantity of potassium hydrosulfide dissolved in alcohol. The latter is prepared by treating an equivalent weight of potassium hydroxide in alcohol with hydrogen sulfide until the cold solution is saturated with the gas, then allowing to stand overnight and filtering. Pour the alcoholic solution of potassium hydrosulfide into the solution of ethyl dithiooxalate with vigorous stirring and allow the mixture to stand for 1 hour. Pour off the supernatant liquid, collect the crystals on a Buchner funnel and wash well with cold alcohol. Dry and store in an amber bottle.

The reagent keeps for several months, but eventually turns to a light brown color. The formation of the characteristic nickel color is accompanied by a turbidity which interferes with accurate readings.<sup>1,4</sup>

**Reactions.** Potassium dithiooxalate gives color reactions or precipitates when added to solutions of most of the heavy metal salts. These reactions, studied by Jones and Tasker,<sup>2</sup> are summarized in Table 27:

The sulfides of most metals form when solutions of the reagent and metallic salts are boiled, or they may form simply on standing.

**Detection and determination of nickel.** The color of nickel dithiooxalate is the most characteristic of any of those formed in the reactions of potassium dithiooxalate with the various metals, and this has been used for the detection and colorimetric determination of nickel. The formula assigned this compound is:



Perhaps iron and cobalt, which give similar colorations, form compounds of the same type.

The sensitivity of the nickel reaction when carried out in a large volume of solution is 1:40,000,000; and when carried out in a test tube is still 1:8,000,000.

The color of the nickel compound is approximately 3 times as intense as that of the permanganate ion. The color reaction of cobalt is as intense as that of nickel. At a dilution of 1:4,000,000, the color intensity is about the same as that produced by adding potassium thiocyanate to a 1:40,000 solution of ferric iron. The sensitivity of the iron reaction is only about 1:100,000.

The deep magenta color obtained in the reaction of potassium dithiooxalate with nickel salts obeys Beer's law over a concentration range suitable for colorimetric determinations. The best results are obtained with a 0.05 per cent solution of the reagent, and with solutions having a nickel concentration of 10 mg. per liter.

Manganese may interfere when present in relatively large quantities, but there is little or no interference in solutions containing less than 15 mg. of

manganese in 50 ml. The quantity of manganese usually present in biological materials is so small as to cause no interference. Iron gives a deep purple color and must be removed. Cobalt interferes, but this interference may be eliminated by a special procedure. Antimony, bismuth, cadmium, cobalt, copper, mercury, silver, tin, palladium, platinum, zinc, cerium, gold, thallium, titanium and vanadium also give color reactions with the reagent. Aluminum, barium, calcium, magnesium, phosphate and strontium may be present.

The color reaction between nickel and potassium dithiooxalate takes place in either neutral or acid solutions. The acidity may vary from 0.0001 to 0.1 M in acetic or hydrochloric acid, but with less than 0.05 mg. of nickel an acidity greater than 0.01 M gives a yellowish-brown color instead of pink.

The following method has been used by Fairhall<sup>4</sup> for the colorimetric determination of small quantities of nickel in tissue, excreta, and foodstuffs:

**Procedure.** Dry the material to be analyzed (tissue, excreta, milk, food-stuffs, etc.) and bake in an oven until charred. Transfer to a porcelain dish and heat until dry, and when dry increase the temperature and carbonize the material. Urine or milk should be boiled to dryness on a hot plate after adding 10 ml. of concentrated hydrochloric acid. Heat the carbonized material at low red heat for not more than 30 minutes. Cool, treat the ash with 15 ml. of 1:1 hydrochloric acid, and filter. Cover the residue with water and heat to boiling after covering the dish with a watch glass. Filter and extract two more times with boiling water. Place the filter and residue in the porcelain dish and again ash in the oven. Cool and extract as before. Three ignitions are usually necessary to dissolve all nickel.

Neutralize the combined hydrochloric acid solutions with 1:1 ammonium hydroxide, using methyl orange as the indicator, and then make the solution just acid with a few drops of hydrochloric acid. Saturate with hydrogen sulfide and allow to stand until precipitation is complete. Filter and wash the residue with water containing hydrogen sulfide. Boil the filtrate to expell all hydrogen sulfide, and add sufficient bromine water to oxidize all iron to the ferric state.

Determine nickel by one of the following methods:

(a) *In the absence of cobalt:* Remove iron by precipitating as ferric phosphate. If phosphate is not present, add a soluble phosphate. The slightly acid solution containing ferric iron is treated with 10 ml. of 50 per cent ammonium acetate solution and 0.5 ml. of glacial acetic acid. The solution must be cold before ammonium acetate is added, since otherwise a part of the iron is reduced. Filter through a quantitative filter paper into a 500-ml. volumetric flask. The filtrate should be water-white and perfectly clear. Dilute to the mark.

(b) *In the presence of cobalt:* Add 10 ml. of 20 per cent sodium citrate solution, and then precipitate calcium by the slow addition of a saturated solution of ammonium oxalate with constant stirring. When all calcium is precipitated, add dilute ammonium hydroxide to precipitate magnesium ammonium phosphate in the same solution. After calcium and magnesium are quantitatively precipitated, filter, wash, and redissolve in hydrochloric acid and precipitate as before.

Filter and combine the two filtrates. Treat with an excess of  $\alpha$ -benzildioxime and filter. Dissolve the residue in aqua regia and evaporate to dryness in a porcelain dish. Add 2 ml. of concentrated hydrochloric acid and again evaporate to dryness to destroy any excess nitric acid. Dissolve the residue in a few drops of dilute hydrochloric acid and dilute to 500 ml.

**Colorimetric comparison.** The solution obtained by either method (a) or (b) is determined as follows: Transfer 50 ml. of the solution to a Nessler tube and add 1 ml. of a 0.1 per cent aqueous solution of potassium dithiooxalate. If nickel is present a clear magenta color develops at once. A brownish color indicates an excess of cobalt, and a purple shade shows that iron has not been completely removed. In the latter case, repeat the oxidation and precipitation with an aliquot of the solution.

Compare the color of the unknown with that of standards prepared by the addition of known quantities of nickel to distilled water containing the same quantities of acid and salts as the sample. In the absence of cobalt, this is 1 g. of ammonium chloride, 1 ml. of 50 per cent ammonium acetate and 1 drop of glacial acetic acid in 50 ml. of standard. In the presence of cobalt, only 1 g. of ammonium chloride and 1 drop of 1:1 hydrochloric acid is added. A suitable series may be prepared containing 0.005, 0.01, 0.02, 0.03, 0.04 and 0.05 mg. of nickel. With larger quantities of nickel, use a colorimeter.

An average error of 2 per cent has been reported for 1 mg. of nickel, with a maximum error of about 5 per cent.

The color changes at different rates with different samples of the reagent. This is inconsequential with less than 0.05 mg. of nickel in 50 ml. at low acidity. In strongly acid solutions, however, the color change is noticeable after an hour or more with the appearance of a turbidity.

1. H. O. Jones and H. S. Tasker, *J. Chem. Soc.* **95**, 1906 (1909).
2. H. O. Jones and H. S. Tasker, *J. Chem. Soc.* **95**, 1904 (1909).
3. J. H. Yoe and F. H. Wirsing, *J. Am. Chem. Soc.* **54**, 1866-76 (1932); *C.A.* **26**, 3203 (1932).
4. L. T. Fairhall, *J. Ind. Hyg.* **8**, 528-33 (1926); *C.A.* **21**, 874 (1927).

## POTASSIUM THIOCARBONATE

Synonym: Potassium sulfocarbonate, potassium trithiocarbonate



Mol. Wt. 186.39

Beil. Ref. III, 221 (87).



**Use:** Detection of nickel, osmium, thallium.

**Determination of nickel.**

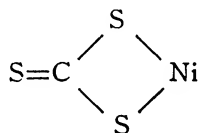
Potassium thiocarbonate is a yellowish-red, deliquescent solid. It is very soluble in water, and the aqueous solution is strongly alkaline. The compound should be stored in a tightly closed container.



**Preparation:** Dissolve 10 g. of potassium hydroxide in 50 ml. of absolute alcohol and saturate the solution with hydrogen sulfide. Then mix with 5 ml. of carbon disulfide dissolved in 50 ml. of absolute alcohol. Filter the precipitate which forms, wash, and dry.

A concentrated aqueous solution of potassium thiocarbonate is prepared as follows: Dissolve 100 g. of potassium hydroxide in 300 ml. of water and saturate with hydrogen sulfide. Add 100 g. of potassium hydroxide, and shake the mixture at 40° C. with 130 g. of carbon disulfide. Add 500 ml. of 95 per cent alcohol. The red liquid which separates contains about 75 per cent of potassium thiocarbonate.<sup>1</sup>

**Detection and determination of nickel.** A rose-red to dark-red or brown color is formed when potassium thiocarbonate is added to an ammoniacal solution of a nickel salt. This reaction is used for the detection and colorimetric determination of nickel.<sup>2-13</sup> The red color is caused by the formation of the nickel salt of potassium thiocarbonate



As little as 0.0085 mg. of nickel in 1 ml. of solution gives a dark red color. The reagent alone gives a yellow color. The following procedure for the determination of nickel in steel has been described by Lindt:<sup>8-10</sup>

**Procedure.** Dissolve 2-5 g. of steel in 50 ml. of 1:1 nitric acid. Add 50 ml. of 1:1 sulfuric acid if necessary. If metals of the hydrogen sulfide group are present, dilute the solution until the acid concentration is about 7 per cent and precipitate with hydrogen sulfide. Filter, oxidize the filtrate with an excess of bromine water, and add a slight excess of ammonium hydroxide to precipitate manganese, iron and aluminum. Boil, cool, and dilute to 1 liter. Filter through a dry filter into a dry receiver.

For the color comparison, use 20 ml. of the solution, or a suitable aliquot diluted to 20 ml. with 1:50 ammonium hydroxide. Most accurate results are obtained with 0.02 to 0.1 mg. of nickel in the solution used for the color comparison, which corresponds to 1 to 5 mg. of nickel in the sample used.

To the 20-ml. portion of the unknown, add 0.5 ml. of a 4 per cent aqueous solution of potassium thiocarbonate and mix. The color develops immediately and is stable for a short time. If the nickel concentration exceeds 0.17 mg. per ml. a precipitate forms in about 4 hours. The color may be determined by dilution, balancing or duplication. For the determination by the dilution or balancing methods, add a suitable quantity of a standard nickel solution containing 0.1 mg. of nickel per ml. to a comparison cylinder and add 0.5 g. of ammonium nitrate dissolved in 1:50 ammonium hydroxide. If sulfuric acid was used in preparing the solution of the sample, add 1 g. of ammonium sulfate. Dilute to 20 ml. with 1:50 ammonium hydroxide and add 0.5 ml. of 4 per cent aqueous potassium thiocarbonate solution. Mix and compare with the sample

similarly and simultaneously prepared. Use 1:50 ammonium hydroxide for the dilution.

For the duplication method, add 0.5 g. of ammonium nitrate and 1.0 g. of ammonium sulfate if sulfuric acid was used in preparing the sample. Dissolve in 18 ml. of 1:50 ammonium hydroxide, and add 0.5 ml. of 4 per cent aqueous potassium thiocarbonate solution. Treat with a standard nickel solution until the colors match. Then adjust the volume to correspond to that of the sample, using more of the standard solution if necessary.

The standard nickel solution is prepared by dissolving 0.6730 g. of nickel ammonium sulfate,  $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  in water and diluting to 1 liter. This solution contains 0.1 mg. of nickel per ml.

Copper, cadmium and other metals of the hydrogen sulfide group interfere, but are removed with hydrogen sulfide. Manganese, iron and cobaltous compounds also interfere. Manganese and iron must be removed, although cobalt does not interfere if oxidized. Zinc yields a white precipitate with potassium thiocarbonate, but this does not interfere if the determination is carried out rapidly. This is important since the separation of zinc from nickel is rather difficult. If a rapid determination is impossible, an amount of zinc equal to that contained in the sample should be added to the standard solution. With a careful control of conditions the method may be used with an accuracy of less than 0.25 per cent of the nickel in steel.

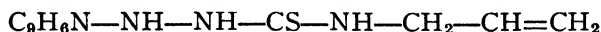
**Detection of thallium.** Thallium thiocarbonate is formed by heating thallous sulfide in an alkaline medium with carbon disulfide. The precipitate which forms is vermilion red and may be used for the detection of thallium at a dilution of 1:50,000. The salt is stable at ordinary temperatures and in the presence of alkalis. The solubility of the thallium salt is about 10 mg. per liter of solution.<sup>14</sup>

**Detection of the platinum metals.** Metals of the iron and platinum groups react with potassium thiocarbonate in a hydrochloric acid solution to give characteristic colors which may be extracted with ether. Osmium yields an olive green color with as little as 0.02 mg. of osmium per ml. of solution.<sup>15</sup>

1. R. Pribram and C. Glucksmann, *Monat.* **13**, 625 (1892).
2. F. D. Snell, *Colorimetric Analysis*, p. 313-4, D. Van Nostrand, New York (1936).
3. K. B. Lehmann, *Arch. Hyg.* **68**, 423 (1911).
4. L. Grunhut, *Z. anal. Chem.* **50**, 313 (1911).
5. M. Lucas, *Bull. soc. chim.* **21**, 432-33 (1899).
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7. M. Lucas, *J. Soc. Chem. Ind.* **18**, 709 (1899).
8. I. v. Lindt, *Z. anal. Chem.* **53**, 165-75 (1914); *C.A.* **8**, 1720 (1914).
9. I. v. Lindt, *J. Chem. Soc.* **106**, II, 298 (1914).
10. I. v. Lindt, *J. Soc. Chem. Ind.* **33**, 335 (1914).
11. G. Loose, *Ing. chim.* **9**, 176-8 (1925); *C.A.* **21**, 1943 (1927).
12. W. Singleton, *Ind. Chemist.* **3**, 121 (1927).
13. J. V. Dubsky, *Mikrochemie.* **28**, 145-72 (1940); *C.A.* **34**, 4686 (1940).
14. M. Picon, *Compt. rend.* **195**, 1274-76 (1932).
15. L. Wohler and L. Metz, *Z. anorg. allgem. Chem.* **138**, 368 (1924); *C.A.* **19**, 621 (1925).

**1-(2-QUINOLYL)-4-ALLYLTHIOSEMICARBAZIDE** $C_{13}H_{14}N_4S$ 

Mol. Wt. 258.30



**Use:** Detection of cadmium, cobalt, copper, mercury, nickel, silver and zinc.

This compound is obtained as colorless crystals by slow crystallization from ether. It is fairly soluble in alcohol, ether and benzene, and is slightly soluble in cold water. It melts at 158° C.

**Preparation:** This reagent is prepared from 10 ml. of allyl isothiocyanate and 16 g. of crystalline 2-quinolyldiazine in ether. Recrystallize from ether.

**Reactions with metals.** When a solution of 1-(2-quinoly1)-4-allylthiosemicarbazide is added to solutions of metal nitrates, yellow precipitates are obtained with cadmium, zinc, and mercurous mercury, and brown precipitates with copper, nickel, cobalt, and silver. Chlorides, bromides, iodides, sulfates, cyanates, and thiocyanates affect the completeness of the precipitation and the appearance of the precipitate.

The test with cadmium is the most satisfactory of those employing this reagent. This is carried out by adding a solution prepared by dissolving 0.5 g. of 1-(2-quinoly1)-4-allylthiosemicarbazide in 100 ml. of 50 per cent alcohol to a solution of cadmium containing a little potassium iodide. With cadmium, a greenish-yellow precipitate is obtained at concentrations as low as one part per million.

1. A. W. Scott and E. G. Adams, *J. Am. Chem. Soc.* **57**, 2541-2 (1935); *C.A.* **30**, 1322 (1936).

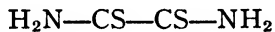
**RUBEANIC ACID**

Synonym: Dithiooxamide

 $C_2H_4N_2S_2$ 

Mol. Wt. 120.19

Beil. Ref. II, 565.



**Use:** Detection of bismuth, cobalt, copper, iron, nickel, and ruthenium.

Determination of copper.

Rubeanic acid is an orange-red crystalline compound. It is slightly soluble in water and cold alcohol, and dissolves with a red color in concentrated sulfuric acid.

**Preparation:** Add ammonia to a concentrated solution of copper sulfate until the precipitate of copper hydroxide redissolves. Cool and add slowly and with continuous stirring, a solution of potassium cyanide until the blue color disappears. Filter, if necessary, and through the filtrate pass a brisk stream of hydrogen sulfide. As soon as a color appears in the liquid cool well. Collect the crystals, wash with cold water and recrystallize from alcohol.<sup>1</sup>

Wollner<sup>2</sup> has prepared rubeanic acid by passing dry cyanogen gas (prepared from copper sulfate and an excess of potassium cyanide) and hydrogen sulfide simultaneously into alcohol.

The alcohol is colored yellow due to the formation of flaveanic acid,  $\text{CN}-\text{CS}-\text{NH}_2$ ; but after a time, and in the presence of an excess of hydrogen sulfide, rubeanic acid is precipitated in the form of a red crystalline solid. This is purified by recrystallizing several times from alcohol.

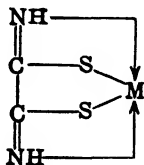
**Reactions with metals.** Rubeanic acid reacts with solutions of zinc, copper, palladium, lead, cobalt, and nickel salts to form rubeanates. These are insoluble in water and, with the exception of lead, are stable at room temperatures. These metals may be determined quantitatively with rubeanic acid, but the accuracy is said not to be great.<sup>18</sup> Ferrous and ferric iron, ruthenium, silver, cadmium and mercury form very unstable rubeanates, which rapidly decompose to form sulfides. Gold and platinum salts are reduced to the metal. Rhodium, magnesium, aluminum, thallium and bismuth do not react.<sup>18</sup>

**Detection of nickel, cobalt and copper.** Rubeanic acid has been used by Ray<sup>3,4</sup> as a sensitive reagent for the detection of nickel, cobalt, and copper. It also gives color reactions with a number of other metallic ions,<sup>5-6,18</sup> and with ferro-aquo ions,  $[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]$  to yield a blue color.<sup>7</sup> According to Wohler,<sup>6</sup> rubeanic acid does not give precipitates with iron salts, and consequently iron does not interfere with the detection of copper or nickel.<sup>4</sup>

Cobalt is quantitatively precipitated as a yellow brown amorphous salt by means of an alcoholic solution of rubeanic acid in the presence of ammonia or of large quantities of sodium acetate. Nickel and copper salts are formed under the same conditions. The nickel compound is blue in color, while the copper salt is black. Rubeanic acid, which is the diamide of dithiooxalic acid, forms in solutions an equilibrium mixture with its tautomeric diimido form.



The acid forms compounds with copper, cobalt and nickel salts to give insoluble complex salts of the following composition:



in which  $M$  = copper, cobalt or nickel. These complex compounds are formed when the concentration of rubeanic acid is great enough to exceed the solubility product of the corresponding rubeanate, and this is made possible by reducing the concentration of the



hydrogen ions, which are formed according to the above equation, by the addition of sodium acetate or an alkali.

The copper, cobalt and nickel compounds, which are precipitated quantitatively from strongly ammoniacal solutions, are also insoluble in dilute mineral acids. The stability of these compounds is exceeded only by that of the cyanide complex salts of the same metals. This is indicated by the fact that the rubeanates are soluble in potassium cyanide, and are not precipitated from alkaline cyanide solutions.

The following procedure may be used for the detection of cobalt:

**Procedure.** Place a drop of the solution to be tested on a strip of filter paper, hold over a bottle of ammonium hydroxide for a short time, and then treat with a 1 per cent alkaline solution of rubeanic acid. A brown spot or ring appears in the presence of cobalt. As little as 0.03 $\gamma$  of cobalt can be detected at a concentration of 1:1,660,000.

A large excess of ammonium salts reduces the sensitivity of this test. Thomson<sup>8,9</sup> has detected as little as 0.002 $\gamma$  of cobalt at a dilution of 1:1,000,000 by means of a coloroscopic method.

An alcoholic solution of rubeanic acid gives a black precipitate of copper rubeanate from an ammoniacal or weakly acid solution of a copper salt. The precipitation of copper with rubeanic acid takes place in ammoniacal or tartrate solutions, but not in alkaline cyanide solutions. This test is extremely sensitive, and may be, under suitable conditions, carried out in the presence of cobalt and nickel salts. The test is given with 0.002 $\gamma$  of copper by using a few drops of a saturated solution of rubeanic acid in ethyl alcohol containing a little isobutyl alcohol.

**Procedure.** Place a drop of nearly neutral solution to be tested on a strip of filter paper, hold over a bottle of ammonium hydroxide and treat with a drop of a 0.5 per cent alcoholic solution of rubeanic acid. A black spot or circle forms if copper is present.

Traces of copper in distilled water give a positive reaction, and so it is necessary in testing for small quantities of copper to compare with a blank prepared using distilled water. By this reaction 0.006 $\gamma$  of copper can be detected at a concentration of 1:2,500,000. In the presence of 400 times as much iron or cadmium, 0.48 $\gamma$  of copper can be detected. In the presence of large quantities of ammonium salts the sensitivity of the reaction is reduced.

Cobalt and nickel salts also give colored compounds with rubeanic acid in neutral, ammoniacal or tartrate solutions. The copper salt, however, is the least soluble of the three, and precipitates from acetic acid solutions when only very small quantities of copper are present. The cobalt and nickel rubeanates are precipitated only very slightly or not at all in the presence of free acetic acid, while under the same circumstances copper is precipitated quantitatively. Since in most instances the nickel or cobalt content of an unknown solution has not been determined, the correct amount of acetic acid necessary to prevent the

precipitation of these metals cannot be determined, and for this reason the test for copper cannot be carried out in the usual way in the presence of cobalt and nickel. By using the principle of capillary separation on filter paper, however, traces of copper can easily be detected in the presence of large quantities of nickel and cobalt.<sup>10</sup>

**Procedure.** Impregnate a strip of filter paper with rubeanic acid and apply a drop of the test solution that has been acidified with acetic acid. Two zones are formed of different acetic acid content: the acid concentration is greatest in the central zone and here copper only is precipitated as an olive green or black circle. The nickel diffuses farther and forms a violet blue ring around the central zone, but this develops further toward the center of the spot as the acetic acid evaporates.

The same process occurs in the presence of cobalt, except that the central ring is surrounded by a yellowish-brown zone of cobalt rubeanate. Copper can be detected when both nickel and cobalt are present. In making this test, the solution should not contain more than 2 per cent of cobalt or nickel. By this test 0.05% of copper can be detected in the presence of 20,000 times as much nickel, and 0.25% of copper can be detected in the presence of 2,000 times as much cobalt.

**Determination of copper.** The black to olive-green color which is formed when rubeanic acid is added to a solution of a copper salt has been used for the colorimetric determination of copper.<sup>19,24</sup> According to British Drug Houses,<sup>25</sup> this reaction is carried out in a solution containing 2 per cent each of free acetic acid and ammonium acetate and 1 ml. of a 0.1 per cent alcoholic solution of rubeanic acid in a total volume of 100 ml. Free mineral acids must be absent, and not more than 0.06 mg. of copper should be present.

Willard and Diehl<sup>26</sup> report that the determination should be carried out at a pH of about 4 and in the presence of gum arabic to stabilize the system. They claim that manganese and zinc do not interfere, but that cobalt and nickel give colors with the reagent.

The following spectrophotometric method is described by Center and MacIntosh:<sup>22</sup>

**Reagents.** *Rubeanic acid solution:* Prepare a 0.1 per cent solution of the reagent in absolute alcohol. This solution is stable 2 or 3 months.

*Acetate buffer:* Mix 400 ml. of glacial acetic acid, 400 g. of pure ammonium acetate, and 200 ml. of distilled water.

**Procedure.** The unknown must be free from mineral acid. Transfer the solution, or an aliquot containing 0.025-0.2 mg. of copper, to a test tube graduated at 50 ml. If the copper concentration is low, use 47 ml. Add 2.5 ml. of the acetate buffer, and then dilute to 49.5 ml. with copper-free distilled water. Then add 0.5 ml. of the rubeanic acid solution, stopper the tube, and invert 4 or 5 times to mix the contents thoroughly.

Read the transmittance within 2 or 3 minutes at a wavelength of 650 or 400  $m\mu$ . Use distilled water as a blank. The copper concentration is determined by reference to a standard curve.

Run a blank on the reagents and distilled water, since small quantities of copper may be present.

The maximum permissible concentrations of other metals is given in Table 28.

TABLE 28.—MAXIMUM PERMISSIBLE CONCENTRATIONS

Metal	Added As	Maximum permissible concentration when measured at 650 $m\mu$ p.p.m.
Mn <sup>+2</sup>	MnSO <sub>4</sub>	6000
Zn <sup>+2</sup>	Zn(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub>	400
Fe <sup>+3</sup>	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ·24H <sub>2</sub> O	250
Fe <sup>+2</sup>	Fe(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	200
Co <sup>+2</sup>	Co(NO <sub>2</sub> ) <sub>2</sub>	60
Ni <sup>+2</sup>	NiSO <sub>4</sub>	40
Ag <sup>+</sup>	AgNO <sub>3</sub>	8
Mn <sup>+7</sup>	KMnO <sub>4</sub>	0

Quandel<sup>11</sup> has used such a method for the determination of copper in steel. By reducing the concentration of the steel solution, and adding a 0.5 per cent gelatin solution as a protective colloid, it is possible to prevent the precipitation of black copper rubeanate, which is obtained as a greenish colloidal suspension. A Zeiss-Pulfrich photometer with a mercury vapor lamp, and a special filter, HG 578, is used. Nickel and cobalt do not interfere with this procedure. Increasing acid concentration weakens the coloration, as do large quantities of ammonium salts. Molybdenum in acetic acid solution has no effect, and vanadium changes the extinction only slightly.

Allport and Skrimshire<sup>12</sup> have used a similar procedure for determining copper in organic materials. Under suitable conditions, copper can be determined in the presence of cobalt, nickel, manganese, lead, bismuth, tin, arsenic and zinc.

Coakill<sup>13</sup> has determined copper in commercial lead. His method includes the following steps:

**Procedure.** Dissolve a 25-g. sample (50 g. if the lead is pure) in 120 ml. of 1:2 nitric acid, and boil to expell the oxides of nitrogen. To the clear, nearly boiling solution of lead nitrate, add 40 ml. of hot 1:3 sulfuric acid. If the solution of the sample in nitric acid is not clear, heat on a sand bath until clear, and filter off the hydrated oxide of tin. Wash the precipitate, and treat the clear filtrate and washings with sulfuric acid. Cool rapidly, and filter on a Buchner funnel. Wash 3 times with 1:15 sulfuric acid, and evaporate the filtrate and washings in a beaker to fumes of sulfur trioxide. Cool, dilute with water, and make up to 100 ml. with water. Transfer 8 ml. of this solution (corresponding to 2 g. of sample) to a Nessler tube, neutralize the free acid with ammonium hydroxide, and then make the solution faintly acid with acetic

acid. Add 0.5 ml. of 10 per cent gum arabic solution and 4-10 drops of a 0.25 per cent alcoholic solution of rubeanic acid, according to the amount of copper present. Compare the resulting color with that of a standard copper solution.

Ringbom<sup>23</sup> has used rubeanic acid for the photometric determination of copper in ores and siliceous roasted ores.

**Detection of nickel.** Nickel can be detected with the aid of rubeanic acid by means of the blue to blue-violet color which forms when the reagent is added to a solution of a nickel salt. The test is carried out by a spot method as follows:

**Procedure.** Place a drop of the solution to be tested on a strip of filter paper, hold over a bottle of ammonium hydroxide, and add 1 drop of a 1 per cent alcoholic solution of rubeanic acid. A blue to blue-violet stain is formed depending upon the amount of nickel present. By this test 0.012% of nickel can be detected at a concentration of 1:1,250,000. The sensitivity of this test is considerably reduced by the presence of ammonium salts.

Despite the fact that rubeanic acid reacts with both cobalt and copper salts, in addition to nickel salts, nickel can be detected in the presence of these metals by using the principle of capillary separation described in the test for copper.<sup>10</sup> This utilizes the difference in the diffusion velocities of metal ammine salts in thin filter paper. The diffusion velocity for nickel is greater than that for copper and cobalt, so that when a drop of the ammoniacal solution of the copper, cobalt and nickel salts is placed on a strip of filter paper, or a drop of the neutral solution on paper is held over a bottle of ammonium hydroxide, the nickel diffuses to the outer zone of the spot. Then when a drop of the alcoholic solution of the reagent is placed beside the test spot so that the two drops merge, a blue ring of nickel rubeanate forms around the brown to green circle, which is due to the cobalt and copper compounds. One drop of a solution containing 1 per cent of cobalt and 0.0021 per cent of nickel still shows a recognizable blue border around the yellowish-brown cobalt spot. In the same way, 0.032% of nickel can be detected in the presence of 4,800 times as much iron.

Wenger and co-workers<sup>14</sup> have studied various tests which have been used for nickel and recommend rubeanic acid as one of the most suitable reagents that has been employed for detection of small quantities of the metal.

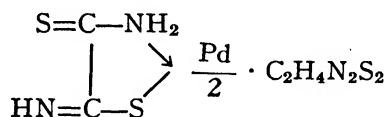
Thanheiser and Waterkamp<sup>15</sup> have used rubeanic acid for the detection of nickel and copper in steel. The surface of the steel is cleaned with emery, then treated with 1-2 drops of mineral acid, and the resulting drop is taken up with filter paper, and tested with an alcoholic solution of rubeanic acid.

**Detection of iron.** Rubeanic acid reacts with ferrous salts in an alkaline solution to form a somewhat unstable blue compound.<sup>16</sup> This reaction appears to be of little value as a test for iron.

**Detection of bismuth.** A saturated alcoholic solution of rubeanic acid gives with an acid solution of bismuth salts an orange-yellow solution. This reaction may be used for the detection of bismuth.<sup>20,21</sup>



**Reactions with the platinum metals.** Rubeanic acid reacts with ammoniacal solutions of copper, cobalt and nickel salts to yield insoluble, colored compounds. In strong mineral acid solutions, however, the reagent reacts only with certain elements of the platinum group.<sup>5,17</sup> Palladium and platinum salts yield red crystalline precipitates, which appear to be inner-complex salts of rubeanic acid. According to Wolbling,<sup>5,17</sup> the formula for the palladium salt, and also for the platinum salt, is represented as follows:



A similar formula has also been assigned to the platinum salt. When rubeanic acid is added to a solution of chloroplatinic acid,  $\text{H}_2\text{PtCl}_6$ , a red coloration is first obtained, and this soon changes to a brownish-red amorphous precipitate.

Ruthenium salts react with rubeanic acid to yield a soluble blue compound, the structure of which has not been definitely determined. It is important to know that osmium, which in its other analytical reactions resembles ruthenium, does not react with rubeanic acid; for this reason rubeanic acid can be used for the detection of ruthenium in the presence of osmium. It is also possible to detect ruthenium in the presence of palladium and platinum by filtering off the insoluble palladium and platinum compounds.

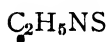
**Procedure.** Acidify the solution to be tested with hydrochloric acid and mix with 1-2 drops of a 0.2 per cent solution of rubeanic acid in glacial acetic acid, and then warm the mixture gently over a microburner. A more or less deep blue coloration appears, depending upon the amount of ruthenium present. By this procedure as little as 0.2 $\gamma$  of ruthenium can be detected at a concentration of 1:250,000.

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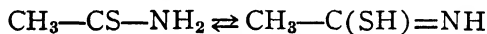
**THIOACETAMIDE**

Synonym: Acetothioamide



Mol. Wt. 75.13

Beil. Ref. II, 232.

**Use:** Detection of bismuth.

Thioacetamide is a crystalline solid melting at 107.5°-108.5° C. It dissolves readily in water and alcohol, but is somewhat less soluble in ether.

**Preparation:** Mix thoroughly 5 molecular weights of acetamide and 1 molecular weight of phosphorous pentasulfide with several volumes of benzene, and heat for a few minutes on a water-bath with shaking. Filter and evaporate the filtrate. The solution solidifies on cooling to give a mass of yellow crystals. These are purified by recrystallizing from benzene.<sup>1,2</sup>

**Detection of bismuth.** Bismuth can be detected in the presence of other metals of the same analytical group by means of the yellow coloration which is produced when a drop of a bismuth solution is treated with an alcoholic solution of thioacetamide. It is probable that the compound  $\text{BiO(SCNHCH}_3\text{)}$  is formed as the result of a reaction between the BiO group and thioacetamide. Cations of the third analytical group and copper also give reactions with this reagent.<sup>3</sup>

1. A. Hantzsch, *Ann.* **250**, 264 (1889).2. A. W. Hoffmann, *Ber.* **11**, 340 (1878).3. N. V. Vavilov, *J. Applied Chem. (U.S.S.R.)*, **11**, 356-62 (1938); *C.A.* **32**, 5725 (1938).**THIOACETIC ACID**

Mol. Wt. 76.11

Beil. Ref. II, 230.

**Use:** Detection of cobalt and lead.

Precipitation of metallic sulfides.

Determination of molybdenum.

Thioacetic acid is a liquid having a penetrating odor of acetic acid and hydrogen sulfide. It boils at  $93^{\circ}\text{C}$ ., and is soluble in water and alcohol.

**Preparation:** Place 300 g. of finely powdered phosphorus pentasulfide and 300 g. of glacial acetic acid in a 2-liter flask, and add 150 g. of glass beads to prevent ignition. Connect the flask to a condenser, and heat the mixture by means of a luminous flame. The acid begins to distill at  $91^{\circ}\text{C}$ . The temperature must not exceed  $100^{\circ}\text{C}$ . during the distillation period. The liquid is redistilled to remove traces of arsenic and antimony.

Ammonium thioacetate, which is commonly used as an analytical reagent, is prepared by pouring a slight excess of 10 per cent ammonium hydroxide into 10 ml. of thioacetic acid. The solution is then diluted to 3 times the volume of the free acid used. This gives a 33 per cent solution. Prepare only enough for immediate use.<sup>1</sup>

**Precipitation of the metallic sulfides.** Schiff and Tarugi<sup>2,3</sup> have recommended the use of a slightly ammoniacal solution of ammonium thioacetate instead of hydrogen sulfide for the precipitation of metallic sulfides. When this reagent is added to an acid solution containing the metals of the hydrogen sulfide group and then heated to  $80\text{--}90^{\circ}\text{C}$ ., all the metals are immediately and completely precipitated as sulfides. This occurs without the accompanying disadvantages of hydrogen sulfide.<sup>8</sup> The reagent may also be used with the rarer elements such as gold, platinum, thallium, vanadium, molybdenum, tungsten, selenium, tellurium, palladium, ruthenium and iridium.<sup>4</sup>

The ammonium salt of thioacetic acid decomposes when heated in an acid medium with the liberation of hydrogen sulfide. Sulfur is not precipitated if an excess of the acid is avoided. The use of this reagent has been suggested in various procedures of systematic analysis of the cations.

**Detection of cobalt.** Danziger<sup>5</sup> has proposed the use of ammonium thioacetate in a sensitive test for cobalt:

**Procedure.** Acidify 5 ml. of the solution to be tested with hydrochloric acid, add a little solid ammonium thioacetate, a few drops of a stannous chloride solution, and an equal volume of amyl alcohol. A mixture of acetone and ether or alcohol and ether may be used. Shake well, and allow the liquid layers to separate. If cobalt is present, the upper layer is colored blue. This reaction is sensitive to 1 part of cobalt in 500,000 parts of solution. The blue compound is thought to be  $(\text{CH}_3\text{—COS})_2\text{Co}\cdot 2\text{CH}_3\text{—CO—SNH}_4$ .

Solid ammonium thioacetate is used in this test to prevent dilution, since water destroys the blue-colored compound. Stannous chloride is added to destroy any ferric ions, since ferric salts yield a red color with the reagent. Amyl alcohol (or other solvent) is used to diminish dissociation and extract the color of the undissociated salt. Amyl alcohol is the most effective of those suggested.

**Detection of lead.** Ammonium thioacetate reacts with lead in a cold hydrochloric acid solution to give a red precipitate of the sulfochloride, which is transformed upon heating into black lead sulfide. Other metals of the hydrogen sulfide group also give colors with the reagent, but lead is the only one to form a reddish sulfochloride.<sup>6</sup>

**Determination of molybdenum.** The following procedure for the determination of molybdenum has been proposed by Herstein:<sup>7</sup>

**Procedure.** Place a solution containing 0.2-0.3 g. of  $\text{MoO}_3$  in a 200-ml. pressure flask, add 5 ml. of concentrated hydrochloric acid, and then add a freshly prepared solution of thioacetic acid containing 0.75 g. of pure acid for each 0.1 g. of  $\text{MoO}_3$ . Digest on a water-bath for 45-60 minutes, cool, and filter through a Gooch crucible using moderate suction. Wash with water containing about 2 per cent hydrochloric acid, and finally wash with a little ethyl alcohol. Dry at  $120^\circ\text{C}$ ., insert the crucible tightly in a perforated asbestos board and heat very gently until all the sulfur is expelled. Gradually increase the heat to dull redness until the precipitate is yellow or grayish and then weigh as  $\text{MoO}_3$ .

Results are claimed to be reliable, and a determination can be made in 3-4 hours.

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## THIOCARBANILIDE

Synonym: Diphenylthiourea, sulfocarbamide

$\text{C}_{13}\text{H}_{12}\text{N}_2\text{S}$

Mol. Wt. 228.30

Beil. Ref. XII, 394.



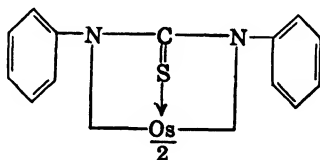
Thiocarbanilide consists of colorless, rhombic plates. It is only slightly soluble in water, but dissolves readily in alcohol and ether. It melts at  $154^\circ\text{C}$ .

**Preparation:** Place 30 g. of aniline, 30 g. of carbon disulfide, and 30 g. of absolute alcohol in a 500-ml. flask, and fit with a reflux condenser. Heat for 8 hours on a water bath. After a time the contents of the flask solidifies. When the reaction is complete, distill off the excess carbon disulfide on a water bath, wash the residue onto a filter with very dilute hydrochloric acid, and then wash with water. Recrystallize from alcohol, and dry the crystals on a porous plate.<sup>1</sup>

**Detection of ruthenium and osmium.** Thiocarbanilide reacts with solutions of ruthenium salts to give a bluish-green coloration, and with osmium salts

to form a red color. These reactions may be used for the detection of osmium and ruthenium.

The following formula for the osmium compound has been proposed



When a solution of ruthenium chloride is heated for a time with thiocarbanilide and hydrochloric acid, a blue-green color is obtained, and this can be shaken out with a little ether. In this way 0.0003 mg. of ruthenium can be detected in 1 ml. of solution. This reaction is 10 times as sensitive as that with thiourea.

When a solution of osmium in concentrated hydrochloric acid is heated two minutes with 0.2 g. of thiocarbanilide, a red coloration appears. The sensitivity of this reaction is increased by extracting the color with ether.<sup>2,3</sup>

Singleton,<sup>4</sup> in a review of the methods of analysis of ruthenium and osmium, recommends the thiocarbanilide reaction.

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## THIOCARBINE

**Use:** Detection of bismuth, copper, lead, mercury, palladium and silver.

The composition of thiocarbine is unknown. Studies reveal, however, that the molecule probably contains the SH group, either as a thioacid or as a thioalcohol.

**Preparation:** Add 10 g. of crystalline sodium thiosulfate to 200 ml. of glycerol at 50° C., and then gradually elevate the temperature to 203° C., during the next 25 minutes. To the hot, dark brown solution add successively 75 ml. of copper-free distilled water and 75 ml. of 2 N sulfuric acid. In each case add the materials in small volumes. Cool the mixture to 70° C., filter 3 times through a thick layer of filter paper on a Buchner funnel, and add 10 ml. of concentrated ammonium hydroxide, and then 10 ml. of an acetic acid solution prepared by diluting 10 ml. of glacial acetic acid with 40 ml. of distilled water. Allow the mixture to stand for 1 week and filter. This solution is used as the reagent.<sup>1</sup>

**Detection of lead, bismuth, copper and palladium.** The following procedure may be used for the detection of lead:<sup>1</sup>

**Procedure.** Place a drop of the solution to be tested on a strip of filter paper, add a drop of the reagent solution, and then add a drop of 0.5 per cent potassium cyanide solution containing 0.5 ml. of ammonia per 100 ml. A red

spot which does not disappear upon treatment with a drop of 1 per cent sodium hydroxide, but which does disappear with 10 per cent sodium hydroxide indicates lead. By this reaction 0.4 $\gamma$  of lead can be detected at a dilution of 1:120,000.

A brown-violet spot is obtained with bismuth, but this dissolves in 1 per cent sodium hydroxide solution. Copper gives a coppery-red spot, and bivalent palladium gives a brown spot. These are stable toward 10 per cent sodium hydroxide, but are unstable toward potassium cyanide. Silver, mercury and cadmium yield less characteristic yellow spots, which dissolve in the cyanide solution.

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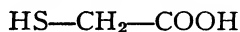
### THIOGLYCOLIC ACID

Synonym: Mercaptoacetic acid

$C_2H_4O_2S$

Mol. Wt. 92.11

Beil. Ref. III, 244.



**Use:** Detection of iron, molybdenum, silver, and tin.

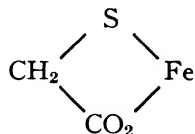
Determination of aluminum, copper, iron, molybdenum and titanium.

Thioglycolic acid is a colorless liquid having a strong unpleasant odor. It has a sp. gr. of 1.325 and boils at 104-106° C. at 15 mm.

**Preparation:** Add 1 mole of chloroacetic acid, dissolved in 5 times as much water, gradually and with shaking to a 15 per cent solution of potassium sulfoxide (KHS) containing 2 moles of the latter. Heat the mixture for 15 minutes on a water-bath and add a concentrated solution containing 1 mole of crystalline barium chloride, and then 1.25 moles of 25 per cent ammonia. Allow the mixture to stand for a few hours, scratch the walls of the vessel, and shake well. Filter off the barium salt, wash with water, and treat with 3 times its weight of 12 per cent hydrochloric acid. Shake out the reagent with 3 portions of ether, remove the ether from the extract by distillation, and finally distill the thioglycolic acid under reduced pressure.<sup>1</sup>

**Detection of iron.** Ferrous salts, even in ammoniacal solutions, give no color reaction with thioglycolic acid if air is excluded, but with ferric iron a blue color appears due to the formation of  $Fe(SCH_2-CO_2H)_3$ . When treated with ammonium hydroxide, the ammonium salt of this acid is formed, and this has a violet-red color. Upon the addition of an excess of ferric chloride, ferric hydroxide is not formed, but instead an ochre-colored salt of ferric ferrithioglycolate is formed, corresponding to the formula,  $Fe_2S_3C_6H_6O_8 \cdot 6H_2O$ .<sup>26</sup> This reaction may be used to detect as little as 0.13 $\gamma$  of iron.<sup>2</sup> If thioglycolic acid is treated with 6 N hydrochloric acid, and then a fairly concentrated solution of ferric chloride is added, the color of the solution is that of ferric chloride. If the solution is diluted with a considerable quantity of water, however, a blue color of ferrithioglycolic acid ( $Fe(SCH_2-CO_2H)_3$ ) appears. This compound is not very stable, and the color soon fades with the formation of ferrous ions and  $(SCH_2-CO_2H)_2$ .

When an alkali hydroxide is added to a solution containing a ferrous salt and thioglycolic acid, in the absence of oxygen or oxidizing substances, a yellow precipitate forms, but this soon disappears. The yellow compound is thought to be:



This reacts with more sodium hydroxide and thioglycolic acid to form  $\text{Fe}(\text{SCH}_2\text{—CO}_2\text{Na})_2$ . In very dilute solutions no color appears, but if the concentration exceeds 0.2 per cent, the solution is yellow to red in color. The addition of methyl alcohol represses the ionization of the sodium salt and changes the color from yellow to red. In addition to the red ferrothioglycolate, an intense red complex exists, which contains 1 atom of ferrous iron and 1 atom of ferric iron, and which has the formula:  $[\text{Fe}(\text{SCH}_2\text{—CO}_2)_2]_2\text{KFe}$ .<sup>3</sup>

The yellow compound which is formed by the action of ferrous salts on the thioglycolic acid is very difficult to prepare in the pure state, since it changes in color rapidly, even in the presence of nitrogen. This compound, as has been described above, dissolves in sodium hydroxide solution to give a soluble complex salt, which is probably  $\text{Fe}(\text{SCH}_2\text{—CO}_2\text{Na})_2$ . If a little perhydrol is added to the alkaline solution containing the red ferrous salt, a color change takes place immediately and upon heating to 60-70° C. ferric hydroxide is precipitated. In addition to oxidizing the iron to the ferric state, hydrogen peroxide converts thioglycolic acid into dithioglycolic acid, thioacetic acid and sulfuric acid.<sup>4</sup>

Andreasch<sup>5,28,29</sup> first observed that iron salts when treated with thioglycolic acid and ammonium hydroxide give an intense red color. This reaction was subsequently confirmed by Claesson<sup>6</sup> and by Ginsberg and Bondzynski,<sup>7</sup> and was later used by Lyons<sup>8,24</sup> and others,<sup>30,31</sup> for the detection of small quantities of iron. Although the color appears due to the formation of ferrous thio-glycolate rather than the ferric salt, the test is independent of the original state of oxidation of the iron, since thioglycolic acid itself is a reducing agent and converts any ferric iron to the ferrous state.

**Procedure.** Add 1 drop of thioglycolic acid to 5 ml. of the neutral or slightly alkaline solution to be tested, and add 5 ml. of concentrated ammonium hydroxide. With ferrous ions an intense red color appears. If ferric ions are present, a transient blue coloration is obtained, but this soon changes to an intense red. This test is obtained with 1 part of iron in 10,000,000 parts of solution, which is reported to be much more delicate than the well-known thiocyanate test.

**Determination of iron.** The reddish-purple color which is obtained in the reaction between thioglycolic acid and solutions of iron salts may be used for the colorimetric determination of iron. The reaction must be carried out in a basic medium, and this is one of the disadvantages of the method. Beer's law is closely followed by the color system, and the color intensity is inde-

pendent of the exact concentration of the reagent and the pH of the solution over the range 6-10. The color is stable for at least 6 hours in diffuse light.<sup>9,10</sup> According to Van Dam,<sup>27</sup> although the color with thioglycolic acid is somewhat more stable, values with thiocyanate are somewhat more reliable when color measurements are made at a definite time after adding the reagent.

Mellon and co-workers<sup>9,11,12</sup> have studied the use of thioglycolic acid for the determination of iron, and report that it is superior to the thiocyanate method, and that thioglycolic acid is more easily used than ferron. Woods and Mellon<sup>12</sup> have found that the color is stable for twelve hours, that it may be developed over a pH range of 7-12, that the effect of change of pH and the effect of adding an excess of the reagent is negligible, and that the development of the color shows a very close conformity to Beer's law. Isbell<sup>13</sup> has used the method of Lyons<sup>8</sup> for the determination of iron as an impurity in cadmium, and reports that cadmium interferes unless a decided excess of ammonia is present.

The following procedure may be used for the determination of iron:<sup>14</sup>

**Reagent.** Dissolve 4 ml. of thioglycolic acid in 8 ml. of concentrated ammonium hydroxide and 50 ml. of water.

**Procedure.** Add 1 ml. of the reagent to the sample to be analyzed and also to a series of suitable standards which have been diluted to about the same volume as that of the unknown. Then add concentrated ammonium hydroxide until a clear purple color is developed. Mix well and compare the unknown with the standards. The pH of these solutions should range from 8-10. If the sample or standards fade before the comparison can be made, restore the color by shaking vigorously with air.

Bismuth, cobalt, lead, mercurous mercury, uranium ( $\text{UO}_2^{++}$ ), gold and silver yield color reactions with thioglycolic acid. The yellow-red color due to cobalt and the orange color of uranium are particularly strong. Manganese gives an amber color when the solution is shaken or stirred, but the color soon fades, and as much as 100 p.p.m. of the reagent does not interfere. Copper, trivalent arsenic, stannous tin, zinc and cadmium bleach the color due to iron, but this effect can be diminished by the addition of more reagent. Very high concentrations of alkali metal salts decrease the intensity of the color. As much as 5000 p.p.m. of chloride, fluoride, tartrate, orthophosphate, oxalate, citrate, and acetate do not interfere. Pyrophosphate in a concentration of 5000 p.p.m. of  $\text{P}_2\text{O}_5$  causes an error of -8 per cent with 1 p.p.m. of iron. Nitrous acid and cyanide must be absent. Molybdate gives a yellow color in relatively high concentrations. Tungsten in quantities greater than 20 p.p.m. as tungstate gives a blue color with the reagent.

Various investigators have used thioglycolic acid for the determination of iron in blood, milk, foods, urine, pharmaceuticals and other biological materials.<sup>15-20,34</sup> Hanzal<sup>16</sup> reports that as much as 500-750 mg. of ortho- or pyrophosphoric acid per 0.1 mg. of iron does not interfere, and this makes possible the determination of iron with thioglycolic acid in biological liquids containing considerable quantities of phosphate.



**Determination of aluminum and titanium in the presence of iron.** Iron can be separated from aluminum in the presence of hydrochloric acid by first reducing the ferric ion with sulfurous acid, then adding thioglycolic acid and ammonium hydroxide. Aluminum is precipitated quantitatively as aluminum hydroxide, and iron is kept in solution as the red ferrous complex. Analogous complexes are formed with nickel, chromium, and zinc, although less readily than with iron.

Iron and titanium can be separated in a manner similar to that used for the separation of iron from aluminum.<sup>4</sup>

**Determination of copper.** Copper is a specific catalyst for the oxidation of thioglycolic acid, thiolactic and thiomaleic acid. These compounds are oxidized by air in a 0.1-1.0 N hydrochloric acid solution in the presence of traces of copper. Thioglycolic acid is oxidized to the disulfide, and the oxidation can be followed by a simple iodometric titration. The amount of acid oxidized is proportional to the time of oxidation for the first 40-50 per cent, but after this the reaction slows down. There is a critical copper concentration which gives a maximum rate of oxidation; below this concentration the rate of oxidation is, within certain limits, proportional to the copper concentration. In thioglycolic acid solutions which are 0.5 N in hydrochloric acid, the critical copper concentration is approximately  $3 \times 10^{-5}$  M and the optimal thioglycolic acid concentration is about 0.05 M. By means of this method quantities of copper ranging down to 0.1  $\gamma$  may be determined with an accuracy of 10-15 per cent. This method is not, however, more satisfactory than Warburg's cysteine method.<sup>21</sup>

**Detection of silver.** Silver may be detected by the precipitate formed in the reaction between silver ions and thioglycolic acid.<sup>32,33</sup> This reaction is capable of detecting 5  $\gamma$  of silver at a limiting concentration of 1:1,000,000.

**Detection and determination of tin and molybdenum.** Clark<sup>22</sup> and Hamence<sup>23</sup> have used thioglycolic acid as a reducing agent for iron to eliminate interference in testing for tin and molybdenum with toluene-3,4-dithiol.

Thioglycolic acid may also be used for the reduction of molybdenum as a preliminary to the extraction with butyl acetate as the thiocyanate complex. This reaction is used for the removal of molybdenum as an interfering substance, and also for the detection and determination of molybdenum. A pink color is formed in the reaction with thiocyanate.<sup>25</sup>

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## THIOGLYCOLIC ACID ANILIDE

$C_8H_9ONS$

Mol. Wt. 167.21

Beil. Ref. XII, 483(265).



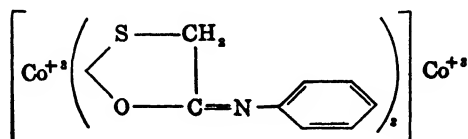
**Use:** Detection of cobalt.

Thioglycolic acid anilide is obtained as crystalline needles from water. It melts at 110.5-111° C. It is very readily soluble in alcohol and ether but is insoluble in benzene.

**Preparation:** Mix 30.4 g. of ammonium thiocyanate and 37.6 g. of monochloroacetic acid in a porcelain dish, and add a solution prepared by mixing 37.2 g. of aniline and 72 g. of alcohol. Warm carefully until the brown-red solution changes in color to a light yellow. Remove the flame and stir vigorously while the crystals are separating. Break the reaction product into small pieces, and wash free of chlorides with distilled water, using suction. Dissolve the residue in concentrated ammonium hydroxide, filter, and precipitate by the addition of hydrochloric acid (methyl orange). Upon acidifying, white crystals of the reagent are obtained.<sup>1,2</sup>

**Detection of cobalt.** If a neutral solution containing cobaltous ions is treated with a little thioglycolic acid anilide, no change is observable, but when the solution is made alkaline with ammonium hydroxide, a voluminous reddish-

brown precipitate forms, which gradually assumes a brownish tinge.<sup>8</sup> The ammonium hydroxide may be replaced with sodium bicarbonate or sodium acetate, but sodium carbonate cannot be used. The precipitate which first forms corresponds to the formula,  $C_{24}H_{24}O_8N_8S_3Co \cdot 4H_2O$ , but upon heating the solution containing this compound the more stable



is formed.

**Reagent.** The reagent is a 2 per cent alcoholic solution of thioglycolic acid anilide. The addition of 0.2 mg. of hydroxyquinoline aids in preserving this solution, and exercises no harmful effect upon the cobalt test.

**Procedure.** In testing for cobalt in the presence of metals of Group III, make the filtrate from the hydrogen sulfide group ammoniacal with ammonium hydroxide, ignoring any precipitate which forms, and boil for 30 seconds to oxidize the cobalt to the trivalent state. Then add a few drops of the reagent and again heat to boiling and make acid with 2 N hydrochloric acid. In case of doubt, add a little ether, whereupon the precipitate collects at the junction of the two liquids. As little as 0.5γ of cobalt can be detected by this method.

The reagent in a slightly alkaline solution gives precipitates with nickel and iron, but these precipitates dissolve in acids while the cobalt compound does not.

The use of thioglycolic acid anilide does not seem suitable for quantitative work unless the precipitate is subsequently converted to a weighable cobalt compound.

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## THIOLACTIC ACID

$C_3H_6O_2S$

Mol. Wt. 106.14

Beil. Ref. III, 289.



**Use:** Determination of copper.

Thiolactic acid is an oily liquid having a very disagreeable odor. It solidifies on cooling and melts at 10° C. It boils at 98.5-99° C. It is miscible with water, alcohol and ether.

**Preparation:** Saturate a 50 per cent aqueous solution of pyroracemic acid at 60-70° C. with hydrogen sulfide. Add concentrated hydrochloric acid as long as any turbidity appears. Reduce the separated compound in a solution weakly

acidified with dilute sulfuric acid by adding 2.5 per cent sodium amalgam with cooling until no more hydrogen sulfide is evolved. The acidified solution of thiolactic acid is then extracted with ether, and the reagent is recovered from the ether extract.<sup>1,2</sup>

**Determination of copper.** Copper catalyzes the oxidation of the thiol acids, and this property can be used as the basis for the microdetermination of copper. Copper appears to be a specific catalyst for the oxidation of the reagent. There is a critical copper concentration which gives a maximum rate of oxidation, but at concentrations below this critical value, the rate of oxidation is, within certain limits, proportional to the copper concentration.<sup>3</sup> Thiolactic acid may be used in a manner similar to that suggested by Warburg<sup>4</sup> in his cysteine oxidation method for copper.

Bjerrum<sup>3</sup> suggests that thiolactic acid may be used in an iodometric method for copper which is similar to that used with thioglycolic acid.

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## THIOMALEIC ACID

Bjerrum<sup>1</sup> reports the use of thiomaleic acid for the microdetermination of copper in a method based on the catalysis of oxidation of thio acids (page 120).

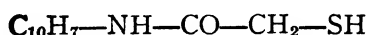
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## THIONALIDE

Synonym: Thioglycolic- $\beta$ -aminonaphthalide

$C_{12}H_{11}ONS$

Mol. Wt. 217.28



**Use.** Determination of arsenic, cadmium, copper, silver, mercury, bismuth, thallium, rhodium, ruthenium, antimony, and lead.

Detection of basicity.

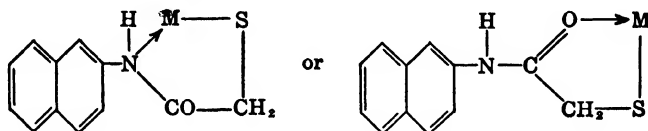
Thionalide consists of white to ivory-colored needles which melt at 109-109.5° C. It is insoluble in water, but dissolves readily in most organic solvents, such as methyl alcohol, ethyl alcohol, acetone, formic acid, acetic acid and pyridine. In water the solubility in 100 ml. is 0.01 g. at 20° C. and 0.08 g. at 95° C. Acetic acid increases the solubility.

**Preparation:** Mix 105.4 g.  $\beta$ -naphthylamine and 240 ml. of ethyl alcohol and reflux until solution is complete. Triturate a mixture of 60.8 g. of ammonium thiocyanate and 76 g. of monochloroacetic acid, and add to the  $\beta$ -naphthylamine solution. Continue to reflux until the mixture hardens to a brown mass. Add water, and grind until the solid turns white. Filter with suction, and wash with large quantities of water until the washings are free from chloride. Discard the filtrate.

Add 400 ml. of methyl alcohol to the residue and reflux for 20 minutes. Decant the liquid and discard. Reflux the residue a second time with a 300-ml. portion of methyl alcohol. Again reflux the gray-colored residue with 400 ml. of methyl alcohol. Filter, and allow the residue to dry in air.

To 18-g. portions of the residue, add 400 ml. of methyl alcohol, 100 ml. of 28 per cent ammonium hydroxide, 20 ml. of water, and 0.15 g. of magnesium ribbon, cut in small pieces. Reflux for 20 minutes in a stream of nitrogen that has been washed in concentrated sulfuric acid. Then add glacial acetic acid, still in an atmosphere of nitrogen, until the pH of the mixture is 5-6. Filter off the precipitate, and pour the filtrate into water. Filter off the yellow-white material and dry. To purify, reflux with ethyl alcohol, filter into a large volume of water, again filter, and dry.<sup>16</sup>

**Reactions with metals.** Thionalide forms stable metal complexes with the metals which yield slightly soluble sulfides. These complexes have the general formula:



Almost all of the metals of the hydrogen sulfide and ammonium sulfide group are precipitated by this reagent in an acetic acid solution.<sup>1,2</sup> On the basis of differences in the degrees of stability and solubility of the complex salts of thionalide, the metals may be separated into four groups: <sup>3,4,12,13</sup>

(I) Metals which are precipitated quantitatively from solutions containing free mineral acid. These include copper, silver, gold, mercury, tin, arsenic, antimony, bismuth, platinum, palladium, rhodium, and ruthenium.

(II) Metals which are precipitated from solutions containing sodium hydroxide and a soluble tartrate. These include copper, gold, mercury, cadmium and thallium.

(III) Metals which are precipitated in a tartrate solution containing potassium cyanide. These include gold, thallium, tin, lead, antimony and bismuth.

(IV) Metals which are precipitated in solutions containing sodium tartrate, potassium cyanide and sodium hydroxide. These include thallium, mercury, lead and bismuth. Mercury, lead and bismuth are precipitated only when present in higher concentrations.

Soares <sup>5</sup> has studied the reaction of various cations with thionalide in different media, and his results are shown in Table 29.

Palladium, platinum, and arsenic show the same behavior in all four solutions, but the precipitates have distinctive colors. The sensitivity of the precipitation reactions of the metals with thionalide is shown in Table 30, which is taken from the work of Berg.

TABLE 29.—REACTIONS OF THIONALIDE WITH THE METALS

Metal	Dil. Mineral Acid	NaOH + tartrate	KCN + tartrate	NaOH + KCN + tartrate
Copper	Precipitates	Precipitates	No precipitation	No precipitation
Silver	Precipitates	Reduces	Reduces	Reduces
Gold	Precipitates	Precipitates	Precipitates	No precipitation
Cadmium	No precipitation	Precipitates	No precipitation	No precipitation
Mercury	Precipitates	Precipitates	Precipitates*	Precipitates*
Thallium	No precipitation	Precipitates	Precipitates	Precipitates
Tin	Precipitates	No precipitation	Precipitates	No precipitation
Lead	No precipitation	Precipitates*	Precipitates	Precipitates*
Arsenic	Precipitates	No precipitation	No precipitation	No precipitation
Antimony	Precipitates	No precipitation	Precipitates	No precipitation
Zinc	No precipitation	No precipitation	No precipitation	No precipitation
Bismuth	Precipitates	Precipitates*	Precipitates	Precipitates*
Palladium	Precipitates	No precipitation	No precipitation	No precipitation
Platinum	Precipitates	No precipitation	No precipitation	No precipitation

\* Precipitation indicated by an asterisk (\*) does not occur if the solution is too strongly alkaline.

TABLE 30.—SENSITIVITY OF PRECIPITATION REACTIONS OF METALS WITH THIONALIDE

(In 0.2 N Mineral Acid Solution)

Metal	Limiting Concentration	Limit of Identification $\gamma$ per ml.	Color of Complex
Antimony	1: 40,000,000	0.02	White
Arsenic	1:100,000,000	0.01	White
Bismuth	1: 10,000,000	0.1	Yellow
Copper	1: 10,000,000	0.1	Yellow
Gold	1: 2,500,000	0.4	Yellowish-brown
Mercury	1: 15,000,000	0.06	White
Palladium	1: 10,000,000	0.1	Yellow
Platinum	1: 10,000,000	0.1	Yellow
Silver	1: 5,000,000	0.2	Yellow
Tin	1: 12,500,000	0.08	White

Since the precipitation of the metals included in the above table is usually quantitative, thionalide can be used for the separation and the determination of most of these cations. Thionalide has many advantages over hydrogen sulfide as a precipitant for the cations: the complexes are precipitated formula pure; and the reagent is more convenient to handle; its large molecular weight practically eliminates weighing error; and there is less coprecipitation. The use of this reagent also permits precipitation from nitric acid solutions.

The precipitation of metals as thionalide complexes makes possible a variety of procedures for the final determination of the metals. The complex may be weighed directly after drying at 105° C.; the metals may be converted to the oxides by ignition; the precipitate may be determined by an iodometric titration or by titration by filtration method; the precipitate may be determined colorimetrically by a reaction based upon the reduction of phosphomolybdic acid; and small quantities of the cations may be determined nephelometrically.<sup>1</sup>

Umemura<sup>10</sup> has studied the proper heating temperature for a number of metal complexes of thionalide, and recommends the values given in Table 31.

TABLE 31.—HEATING TEMPERATURE OF METAL COMPLEXES OF THIONALIDE

Complex	Heating Temperature	Complex	Heating Temperature
PtT <sub>4</sub>	<170°	BiT <sub>3</sub>	140-160°
PdT <sub>3</sub>	<195°	SbT <sub>3</sub>	<200°
AuT <sub>3</sub>	<230°	CdT <sub>3</sub>	<210°
CuT <sub>2</sub> ·H <sub>2</sub> O	Room temperature	TiT	<220°
CuT <sub>3</sub>	140-200°	PbT <sub>3</sub> ·H <sub>2</sub> O	Room temperature
AgT	<190°	PbT <sub>3</sub>	100-145°
BiT <sub>3</sub> ·H <sub>2</sub> O	Room temperature		

Where HT = Thionalide.

**Determination of copper.** When a freshly prepared alcoholic or acetic acid solution of thionalide is added to a slightly acid solution of a copper salt, the copper is quantitatively precipitated as  $\text{Cu}(\text{C}_{12}\text{H}_{10}\text{ONS})_2 \cdot \text{H}_2\text{O}$ .<sup>6</sup> The water of hydration is not removed by drying at  $105^\circ\text{C}$ . Precipitation is carried out in a dilute nitric or sulfuric acid solution having a maximum acidity of 0.5 N. In 0.1 N acid solutions, the presence of as much as 1 per cent chloride does not cause appreciable error, but greater quantities cause negative errors. If the concentration of the acid is as great as 0.5 N, results are too high in the presence of chlorides. The following procedure is recommended for the copper precipitation:

**Procedure.** Heat the copper solution to  $80\text{--}85^\circ\text{C}$ . and add with stirring an alcoholic or acetic acid solution of thionalide. Use a 10-fold excess of the reagent. For example, use 20 ml. of a 1 per cent thionalide solution for a sample containing 20 mg. of copper in a volume of 150 ml. Coagulate the precipitate by stirring, and filter hot through a glass filter crucible which is warmed with hot water before filtration. Wash the precipitate free of acid with hot water, and dry at  $105^\circ\text{C}$ . to constant weight. The factor for copper is 0.1237.

Since thionalide is a weak reducing agent, it is important that oxidizing agents such as ferric chloride be destroyed before precipitation, and this is readily effected by means of hydroxylamine sulfate.

Results with this method are said to be excellent.

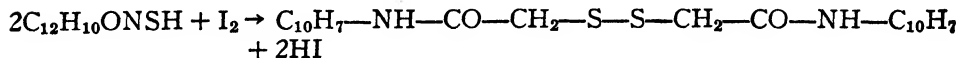
By the above procedure copper can be separated satisfactorily from iron, thallium, lead, aluminum, chromium, nickel, manganese, cobalt, zinc, magnesium, cadmium, calcium and barium.

To separate copper from metals not precipitated by thionalide in acid solution, the volume of the sample solution should be approximately 200–300 ml.

To determine the metals present in the filtrate after filtering off the copper thionalide complex, warm to  $70\text{--}80^\circ\text{C}$ ., and add dropwise with stirring an approximately 0.5 N iodine-potassium iodide solution until the yellow color is permanent. Cool to room temperature, and filter off the precipitate of dithionalide. Determine the metals in the filtrate by any suitable method.

It is not practicable to reduce oxidizing substances in the presence of chlorides, and in such cases it is best to remove the chloride by fuming with sulfuric acid. The cooled solution is then diluted with water and treated as described above.

Thionalide reacts with free iodine according to the following equation



to form the slightly soluble dithionalide. This reaction proceeds quantitatively, and can be used for the indirect determination of copper and other metals after precipitation with thionalide.

**Procedure.** Precipitate copper as described above, and filter through a filter wet with hot water. Wash free of acid with hot water, and then transfer the filter and precipitate to the beaker in which the precipitation was carried out. Add 50 ml. of glacial acetic acid, 4–5 ml. of 5 N sulfuric acid, and about



0.1 g. of potassium iodide, and 10 ml. of 1 N ammonium thiocyanate, and stir well. Then add an excess of 0.02 N iodine solution, dilute with water, and titrate the excess iodine with 0.02 N sodium thiosulfate. The solution may be titrated potentiometrically.<sup>8</sup> One ml. of 0.02 N iodine solution = 0.6357 mg. of copper.

When the thionalide complex of copper is oxidized with hydrogen peroxide in a potassium hydroxide solution, the side chain of the organic compound is destroyed and the potassium salt of an organic acid of unknown composition is formed. By using a measured excess of standard potassium hydroxide, and titrating with standard hydrochloric acid the excess remaining after the formation of the salt, the quantity of copper in the complex can be calculated.

Berg and co-workers<sup>11</sup> have used thionalide for the nephelometric determination of small quantities of copper.

**Procedure.** To 15 ml. of the copper solution add 5 drops of 5 N sulfuric acid, and heat to boiling. Then add 3 drops of a 1 per cent solution of thionalide in glacial acetic acid. Compare the resulting turbidity with that produced by standards similarly treated and containing known quantities of copper.

**Determination of silver.** Silver is precipitated with thionalide in a manner similar to that described for copper. The precipitation of silver from pure solutions of its salts, however, offers no advantages over methods commonly in use. On the other hand the reagent is recommended for the separation of silver from lead and palladium.<sup>6</sup> Silver is precipitated exactly as described for copper, but the thionalide complex cannot be weighed directly, since it is decomposed by drying at 100° C. Best results are obtained by filtering through paper, igniting at red heat to metallic silver, converting to silver chloride and weighing in that form.

Silver may be determined titrimetrically, as in the method described for copper, except that the thiocyanate is not used. One ml. of 0.02 N iodine solution corresponds to 2.158 mg. of silver.<sup>8</sup>

Small quantities of silver may also be determined nephelometrically as described for copper.

**Determination of mercury.** By carefully following specified conditions, mercury is precipitated with thionalide as  $\text{Hg}(\text{C}_{12}\text{H}_{10}\text{ONS})_2$ . These conditions are:<sup>6</sup>

(1) The chloride ion concentration of the solution must not exceed 0.1 N, since otherwise results are too high.

(2) Mercuric nitrate must be converted to the chloride by adding to the solution a quantity of chloride equivalent to the amount of mercury present. Sulfates do not interfere.

(3) Use a 3-fold excess of thionalide for the precipitation.

Carry out the precipitation as described for copper, filter through a warmed filter crucible, and dry the precipitate at 105° C. The factor for mercury is 0.3169.

For the iodometric titration of mercury, follow the same directions given for silver. This method is said to be very exact.

**Determination of lead.** Lead is precipitated with thionalide from a solution made alkaline with sodium carbonate and containing cyanide and tartrate. The bright yellow precipitate formed in this way corresponds in composition to the formula  $\text{Pb}(\text{C}_{12}\text{H}_{10}\text{ONS})_2$ . This reaction is particularly useful for the separation of lead from ferric iron, aluminum, cobalt, nickel, silver, zinc and copper. Cadmium, trivalent arsenic, trivalent chromium, and tetravalent titanium do not interfere with the precipitation.<sup>7</sup>

The separation is carried out as follows:

**Procedure.** To the acid solution to be analyzed, containing no sulfate, add 10-20 ml. of 20 per cent sodium tartrate solution, and sufficient 2 N sodium carbonate solution to make the solution neutral to phenolphthalein. Add sufficient 20 per cent potassium cyanide solution to form complex ions with interfering cations (40-50 ml. for a 0.5 g. sample), and then additional sodium carbonate to make the solution about 1 N in alkali. Then to 100-300 ml. of the solution, add 6-8 times as much thionalide as there is lead present. The reagent is dissolved in about 50 times as much ethyl alcohol. Heat gently to boiling and allow to stand for a little while. Filter the cold solution through a G 4 filter crucible, and wash with cold water until free from cyanide, and then with 50 per cent acetone until free of excess reagent. This is indicated when a portion of the filtrate, diluted to 4 times its volume, does not show any turbidity when acidified with sulfuric acid and treated with several drops of 0.1 N iodine solution. Dry the washed precipitate at 105° to constant weight. The factor for lead is 0.3240.

For satisfactory results, the chloride ion concentration must not exceed 4 per cent, and the sulfate ion concentration must be less than 1 per cent.

**Determination of bismuth.** Bismuth is precipitated from a nitric or sulfuric acid solution with thionalide. The complex first forms as a milky precipitate, and cannot be filtered until it has been heated for 30 minutes on a water bath. The acid concentration most favorable for the coagulation of the precipitate is 0.1 N. In the presence of chlorides or sulfates, however, a 0.2 N mineral acid solution is necessary to prevent precipitation of the basic bismuth salt.

In nitric acid solutions which are free of chloride and sulfate, precipitate bismuth as follows: <sup>6</sup>

**Procedure.** Add ammonium or sodium hydroxide to the bismuth solution to the appearance of a permanent turbidity, and add 3-5 ml. of 2 N nitric acid. Dilute the mixture to 100 ml. and precipitate as described for copper, using a 4-fold excess of the reagent. Cover the beaker in which the precipitation is carried out, and heat for 30 minutes on a water bath with frequent shaking. When the supernatant liquid becomes clear, filter the precipitate through a warmed filter crucible, wash, and dry to constant weight at 100° C. The precipitate corresponds to the formula  $\text{Bi}(\text{C}_{12}\text{H}_{10}\text{ONS})_3 \cdot \text{H}_2\text{O}$ . The factor for bismuth is 0.2387.

If the acid bismuth solution contains chloride and sulfate, neutralize with ammonium or sodium hydroxide, add 10 ml. of 2 N sulfuric or nitric acid, dilute to 100 ml. with water, and precipitate as described above. Immediately after precipitation, neutralize the solution by adding 5 ml. of 2 N sodium hydroxide for each 100 ml. of solution. Finally, treat the precipitate as described above.

The bismuth determination is not satisfactory if large quantities of chloride are present.

Special precautions are necessary for the separation of bismuth from large quantities of lead. Dilute the neutralized solution to about 200-400 ml., add 5-6 ml. of 2 N nitric acid for each 100 ml. of solution, and precipitate bismuth with thionalide as described above. If ferric salts are present, the iron must be reduced in the usual manner. In the bismuth determination, however, a part of the iron is oxidized during the heating period on the water bath, and the ferric salt so formed oxidizes a part of the reagent to insoluble dithionalide. For this reason the precipitate of the bismuth complex cannot be weighed after filtering and drying. The recommended procedure is carried out as follows: filter the precipitate through a paper filter, dry at 100° C., ash the paper separately in a weighed porcelain crucible, and then transfer the remaining precipitate to the crucible. Add 1-2 g. of oxalic acid and ignite, first over a small flame, and then 5 minutes with the full Bunsen flame.

In an alkaline solution, bismuth is precipitated by thionalide as a bright yellow complex corresponding in composition to  $\text{Bi}(\text{C}_{12}\text{H}_{10}\text{ONS})_3$ , which does not contain any water of hydration, and which is suitable for weighing. Bismuth can be separated from aluminum, titanium, chromium, cobalt, zinc, nickel, platinum, iron, palladium, cadmium, mercury, arsenic, silver, and copper by precipitating with thionalide from a solution made alkaline with sodium carbonate, and containing tartrate and cyanide. The precipitation is very similar to that of lead. Since the bismuth thionalide complex is very soluble in acetone, the precipitate is washed free of cyanide with cold water, then washed with small portions of 10 per cent alcohol until the filtrate shows no turbidity when tested with an iodine solution, and finally dried at 105° C. and weighed. The factor for bismuth is 0.2436.

If large quantities of accompanying metals are present, dissolve the precipitate in acetone, add 100 ml. of a 5 per cent potassium cyanide solution containing 2 g. of sodium tartrate, and remove the acetone by boiling. Cool, and proceed as described above.

Bismuth can be determined by an iodometric titration method, but the procedure must be modified by adding pure, iron-free ammonium chloride to the solution before the titration. The solution must remain saturated with ammonium chloride.

Bismuth can be determined by a titrimetric method, using the filtration-titration technique for determining the end point. A 1 per cent solution of thionalide in glacial acetic acid is used, and this is standardized empirically against a known quantity of bismuth as follows:

**Procedure.** Adjust the acidity as described above for the precipitation of bismuth, and heat to 80-90°. Allow the reagent to flow from a buret into the hot solution until a filtered portion yields no further turbidity when treated with an additional drop of the reagent. In this way an approximate factor for the reagent solution is obtained. An exact value is obtained by a second titration, using very small drops at the end point. In this titration, pour the solution several times through the same filter and then titrate, since otherwise errors may arise through adsorption of traces of metallic ions by the filter paper.

Berg and co-workers<sup>11</sup> have used thionalide for the nephelometric determination of small quantities of bismuth. The method is similar to that described for copper.

When the bismuth thionalide complex is oxidized with hydrogen peroxide in a potassium hydroxide solution, the side chain of the organic part of the complex is destroyed, and the potassium salt of an organic acid of unknown composition is formed. By using a measured excess of a standard potassium hydroxide solution, and titrating with a standard solution of hydrochloric acid the excess remaining after the formation of the potassium salt, the quantity of bismuth in the complex can be calculated.

**Determination of antimony.** Antimony is precipitated with thionalide as the complex,  $\text{Sb}(\text{C}_{12}\text{H}_{10}\text{ONS})_3$ . The sensitivity of this precipitation is about 1:2,500,000. Antimony is precipitated under the same conditions as described for lead, but in the antimony determination, as in the bismuth determination, the precipitate must be washed with 10 per cent alcohol. The factor for antimony is 0.1581. This method is useful for the separation of antimony from cobalt, ferrous iron, trivalent cerium, trivalent chromium, and tetravalent titanium. Lead, tin, bismuth, gold, and thorium must be absent, and arsenic, cadmium, mercury, and the alkaline earth metals also interfere.<sup>7</sup>

**Determination of thallium.** Since thallium alone is precipitated in a solution containing sodium hydroxide, sodium tartrate, and potassium cyanide, thionalide is a specific reagent for this metal. The thallium complex is precipitated as a lemon-yellow, crystalline compound, which is insoluble in acetone, and has the formula,  $\text{Tl}(\text{C}_{12}\text{H}_{10}\text{ONS})$ . The sensitivity of the precipitation reaction is 1:10,000,000.

By properly controlling conditions, thallium can be separated from aluminum, antimony, arsenic, bismuth, cadmium, cobalt, copper, gold, lead, mercury, molybdenum, nickel, palladium, platinum, silver, tellurium, tin, tungsten, uranium, vanadium, and zinc.<sup>3</sup>

Thallium is precipitated from pure solutions of its salts by the following procedure:

**Procedure.** Neutralize the acid solution containing 0.025-0.1 g. of thallium with 2 N sodium hydroxide solution, and add 2 g. of sodium tartrate and 3-5 g. of potassium cyanide. Then make the solution alkaline by adding 10-20 ml. of 2 N sodium hydroxide solution. Dilute the mixture to 100 ml.

and add 4-5 times the theoretical quantity of thionalide dissolved in a little acetone. Heat to boiling with stirring, and allow the mixture to cool to room temperature. Filter through a G-4 glass filtering crucible. Wash the precipitate with cold water until free from cyanide, and then wash free of thionalide with acetone. Dry at 100° C. and weigh. The factor for thallium is 0.4860.

The precipitate may be dissolved in a mixture of 3 parts of glacial acetic acid and 1 part of 2 N sulfuric acid by volume, treated with a measured volume of standard 0.02 N iodine solution, and the excess titrated with 0.02 N sodium thiosulfate solution. One ml. of 0.02 N iodine solution = 4.09 mg. of thallium.

Still a third method for determining thallium is based upon treating the washed precipitate of the thallium complex with concentrated sulfuric acid to oxidize the organic matter, and then titrating the thallium potentiometrically by a bromometric method.<sup>9</sup>

Ferric iron and gold, platinum and palladium must be reduced to their lowest valence or they will cause an oxidation of thionalide. Vanadium must also be reduced to the vanadyl salt, and when cadmium is present a greater quantity of potassium cyanide must be added. If uranyl salts are present, sodium uranate may precipitate with the thallium, but this can be dissolved in a solution of ammonium carbonate. Mercury, bismuth and lead are precipitated with thallium in the above procedure, but the complexes of these metals are so soluble in acetone that interference from this source can be prevented by using a 10-fold excess of thionalide dissolved in so much acetone that 30 per cent by volume of acetone is present during the precipitation.

In general, it is essential in separation procedures that not more than 5 g. of potassium cyanide and 5 g. of sodium tartrate be present in 100 ml. of solution. In the presence of other metals, such as cadmium, zinc, cobalt, nickel, copper, silver, mercury, and gold, it is necessary that the quantity of potassium cyanide used be sufficient to form metal complexes. Also, in such cases, the hydroxyl ion concentration is lowered, and must be adjusted to 1 N by adding more 2 N sodium hydroxide.

Thallium may be determined by a colorimetric method based on the reducing action of thionalide upon the heteropoly molybdenum and tungsten acid of phosphorus to form the blue reduction product.<sup>11</sup>

**Reagents.** *Phosphotungstomolybdic acid:* Mix 1 g. of phosphomolybdic acid, 5 g. of sodium tungstate, 5 ml. of phosphoric acid and 18 ml. of water, and heat for 2 hours under reflux. Dilute the resulting solution to 25 ml. The reflux condenser should be attached to the flask by means of a ground glass joint.

**Procedure.** To 2-3 ml. of a neutral solution of the thallium salt, add 0.5 ml. of 2 N sodium hydroxide and 0.5 ml. of 10 per cent potassium cyanide. Then precipitate thallium by adding to the cold solution 5-6 drops of a 5 per cent solution of thionalide in acetone and mix in a centrifuge tube. Heat for 5 minutes at 90° C. with constant stirring. This causes the precipitate to become crystalline and deep yellow in color. Cool, centrifuge, and wash twice with 3-5 ml. portions of acetone. Dissolve the precipitate by the addition of 2 drops of N sulfuric acid and 1 ml. of alcohol. Transfer the solution to a colorimeter

with the aid of warm alcohol and water, and add 1-3 drops of the phosphotungstomolybdic acid reagent and 30-40 drops of formamide. Shake thoroughly, allow to stand for 15 minutes at 40° C. and compare the resulting color with that obtained with standards similarly treated.

Results obtained with 0.005-0.300 mg. of thallium are reported as excellent.

Other metals precipitated by thionalide can be determined in a similar manner, except that the precipitate is washed with hot water and dissolved in pyridine.

**Nephelometric determination of metals.** Berg and co-workers<sup>11</sup> have used thionalide for the nephelometric and colorimetric determination of small quantities of copper, mercury, silver, thallium, antimony, arsenic, tin, gold, palladium, and bismuth.

**Procedure.** To 15 ml. of a solution containing the element to be determined, add 5 drops of 2 N sulfuric acid, heat to boiling, and add 3 drops of 1 per cent thionalide in glacial acetic acid. Compare the resulting turbidity with that produced by known quantities of the element.

**Determination of the platinum metals.** Thionalide reacts with various metals of the platinum group to yield colored precipitates. This behavior has been utilized by Kienitz and Rombock<sup>12</sup> for the microdetermination of rhodium. If a solution of rhodium chloride is treated at the boiling point with an acetic acid solution of thionalide, an orange precipitate of  $\text{Rh}(\text{C}_{12}\text{H}_{10}\text{ONS})_3 + \text{RhCl}_3$  is formed. If the solution is first heated with sulfuric acid to remove all chloride, the precipitate is not contaminated with the excess rhodium as rhodium chloride, but forms as  $\text{Rh}(\text{C}_{12}\text{H}_{10}\text{NOS})_3$ . The precipitate is practically insoluble even in hydrochloric acid. Rhodium is conveniently determined by means of a procedure based on the following operations: Add to the rhodium solution a known quantity of a freshly standardized solution of thionalide in acetic acid, filter off the precipitate while the solution is still hot, wash with a little glacial acetic acid, and determine the excess reagent by an iodometric determination. In determining 0.25-7.5 mg. of rhodium, the greatest error in a series of five determinations was 0.23 mg.

**Procedure.** Mix about 30-50 ml. of a chloride-free rhodium solution, containing 0.25-10.0 mg. of the metal, with an excess of a standardized, 1-2 per cent solution of thionalide in acetic acid. Heat to boiling, filter hot, and wash the orange-yellow precipitate with a few ml. of glacial acetic acid. Titrate the excess thionalide in the filtrate with a standard iodine solution, using a slight excess, and then titrate the excess iodine with a thiosulfate solution. Determine the thionalide content of the reagent solution by titrating in the same manner. One ml. of 0.01 N iodine solution = 0.343 mg. of rhodium.

Rogers and co-workers<sup>13</sup> have used thionalide for the determination of ruthenium. Ruthenium tetroxide is distilled from a dilute sulfuric acid solution containing sodium bromate, and is then absorbed in a 3 per cent solution of hydrogen peroxide (free from acetanilide), and the ruthenium is recovered by precipitation with thionalide from a hydrochloric acid solution. Precipitation is

complete in a solution which is 0.2-0.5 N in hydrochloric acid. The precipitate is ignited, first in air, and finally in hydrogen, and weighed as metallic ruthenium.

**Procedure.** *Absorption of ruthenium tetroxide:* Transfer the sample containing about 10 mg. of ruthenium to a distillation flask, and dilute to a volume of approximately 200 ml. Connect the flask to a train of 2 absorption flasks, which are cooled in ice, and to the first flask add 35 ml. of 3 per cent hydrogen peroxide, and to the second flask add 15 ml. of hydrogen peroxide. Add to the distillation flask 25 ml. of 10 per cent sodium bromate solution, and boil gently to remove the ruthenium tetroxide. Boil for 2 hours to transfer the ruthenium completely to the hydrogen peroxide solutions.

*Determination of ruthenium:* Wash the total hydrogen peroxide absorbent into a 150-ml. beaker. Add about 0.6 ml. of hydrochloric acid and boil until a gas is no longer evolved. Weigh out an excess of the calculated amount of thionalide necessary, dissolve in about 3 ml. of alcohol, and add to the ruthenium solution by means of a glass capillary. Boil until the precipitate is coagulated, filter through a 7-cm. Whatman No. 42 paper, and wash thoroughly with hot water. Transfer the paper and precipitate to a porcelain crucible and char, and then burn off the carbon. The ignition period lasts only about two minutes. Reduce the residue in hydrogen, cool in hydrogen, and weigh as metallic ruthenium.

**Determination of basicity in slightly soluble materials.** Feigl and da Silva<sup>14</sup> have used thionalide in one of the reagents for detecting basicity in slightly soluble materials. The following procedure is used:

**Reagents.** (a) Mix 50 ml. of 4 per cent nickel nitrate solution with 100 ml. of a 1 per cent alcoholic solution of dimethylglyoxime.

(b) Mix 50 ml. of 4 per cent cupric nitrate solution with 100 ml. of 1 per cent benzoinoxime in ethyl alcohol.

(c) Mix 50 ml. of 4 per cent nickel nitrate solution with 100 ml. of 1 per cent thionalide in ethyl alcohol.

Heat the above mixtures for a short time on a water-bath and filter. In this way 3 reagents are prepared containing nickel or copper ions, an excess of the organic reagent, and a low hydrogen ion concentration corresponding respectively to pH 1.9, 1.6 and 2.9.

**Procedure.** If the free acid in the above reagents is neutralized by any base, the nickel or the copper ions are precipitated as red nickel dimethylglyoxime, green copper benzoinoxime or dark-brown nickel thionalide. To make a test for basicity proceed as follows: Place 0.5-1.0 mg. of a slightly soluble material to be tested on a white spot plate and add 1-2 drops of any one of the above reagents. A positive color test is obtained if the solution is basic.

Such solids as barium oxide, barium carbonate, calcium oxide, calcium carbonate, calcium phosphate, and magnesium oxide give a positive test.

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## THIOUREA

Synonym: Thiocarbamide

$\text{CH}_4\text{N}_2\text{S}$

Mol. Wt. 76.12

Beil. Ref. III, 180.

$\text{NH}_2\text{—CS—NH}_2$

**Use.** Detection of antimony, bismuth, cadmium, ferricyanide, germanium, lead, osmium, ruthenium, selenium and tellurium.

Determination of bismuth, bromate, cadmium, chlorate, chromate, copper, lead, manganese dioxide, mercury, nitrite, osmium, perborate, percarbonate, peroxide, ruthenium, thallium and zinc.

Thiourea is a white crystalline solid which melts at 180-182° C. It is fairly soluble in water and alcohol, but is sparingly soluble in ether. It is neutral in its reaction.

**Preparation:** Heat ammonium thiocyanate in an enameled iron dish until small bubbles of yellow foam appear, and there is a marked evolution of ammonia, carbon disulfide and hydrogen sulfide. Cool the mass by gradually adding a little cold water. Remove the excess ammonium thiocyanate from the solidified mass by extracting with cold alcohol. Purify the product by recrystallizing from hot water.<sup>1,2</sup>

**Reactions of thiourea with metals.** Thiourea reacts with a number of cations and anions to give color reactions of analytical importance. A summary of these reactions, investigated by Yoe and Overholser,<sup>51</sup> is given in Table 32.

**Detection of bismuth.** Acid solutions of bismuth salts react with thiourea to give a deep yellow color. Brown-yellow to orange-red crystalline compounds have been isolated from such solutions, depending upon the conditions under which the reactions take place. If a solution of bismuth nitrate is acidified with a few drops of nitric acid and then treated with a 15 per cent solution of thiourea, brownish-yellow needles having a composition corresponding to



1 mole of bismuth and 1 mole of thiourea (m.p. = 149° C.) are obtained. A bright yellow crystalline solid, corresponding to 1 mole of bismuth and 2 moles of thiourea (m.p. = 153° C.) and bright glistening brownish-yellow needles corresponding to 1 mole of bismuth and 3 moles of thiourea (m.p. = 151° C.) are also formed.<sup>3</sup>

TABLE 32.—REACTIONS OF THIOUREA WITH METALS

Ion	Medium	Reaction
Ag <sup>+</sup>	Neutral	Tan precipitate
Ag <sup>+</sup>	Ammoniacal	Black precipitate
Bi <sup>3+</sup>	Acid	Bright yellow color
Ce <sup>4+</sup>	Acid	Decolorized
Cu <sup>+</sup>	Ammoniacal	Brown precipitate
Cu <sup>2+</sup>	Acid	White precipitate
Fe <sup>3+</sup>	Acid	Light pink color
Hg <sub>2</sub> <sup>2+</sup>	Acid	Gray precipitate
IrCl <sub>6</sub> <sup>-2</sup>	Acid	Decolorized
OsO <sub>6</sub> <sup>-2</sup>	Neutral	Brown color
OsO <sub>5</sub> <sup>-2</sup>	Acid	Red color
OsO <sub>5</sub> <sup>-2</sup>	Ammoniacal	Gray color
Pd <sup>2+</sup>	Acid and Ammoniacal	Yellow color
PtCl <sub>6</sub> <sup>-3</sup>	Ammoniacal	Brown color
RuCl <sub>4</sub> <sup>-</sup>	Acid	Dark greenish-blue color
Sb <sup>3+</sup>	Acid	Pale yellow color
SeO <sub>3</sub> <sup>-2</sup>	Acid	Red precipitate
Tl <sup>+</sup>	Neutral	White precipitate
Tl <sup>+</sup>	Acid	Heavy white precipitate

The color reaction between bismuth salts and thiourea has been used by various investigators for the detection of bismuth.<sup>4-14,48</sup> According to Dubsy and co-workers,<sup>14</sup> as little as 1γ of bismuth can be detected in 30,000 parts of solution, while West and Tokos<sup>57</sup> reports the sensitivity as 1.5γ at a dilution of 1:100,000. Bismuth in a nitric acid solution can easily be detected by means of thiourea in the presence of low concentration of silver, lead, mercurous, mercuric, copper, arsenic, antimony, tin, aluminum, zinc, manganese, calcium, strontium, magnesium, barium, ammonium, potassium, sodium, chloride, sulfate and phosphate ions. If mercurous salts are present, a grayish precipitate is first formed and this must be filtered before observing the bismuth test. If colored cations such as iron, nickel, cobalt and chromium are present in large quantities, it is necessary first to precipitate with hydrogen sulfide, then dissolve the sulfides in 1:1 nitric acid, heat and filter off any sulfur formed, and then detect bismuth in the filtrate.<sup>13</sup> Antimony also gives a yellow color with bismuth. Fluoride destroys the color caused by antimony, but not that due to bismuth.

West and Tokos<sup>57</sup> have studied the effect of various ions on the bismuth test with thiourea, and have summarized their results as follows:

(a) *Positive interference*: Sb<sup>3+</sup>, Pd<sup>2+</sup>, VO<sub>3</sub><sup>-</sup>, TeO<sub>3</sub><sup>-2</sup>.

(b) *Negative interference*: None.

(c) *Masking interference*:  $\text{Hg}^+$  (black),  $\text{SeO}_3^{-2}$  (red),  $\text{SeO}_4^{-2}$  (red),  $\text{Os}^{+8}$  (brown to pink), and colored ions, such as  $\text{Cr}^{+3}$ ,  $\text{Cr}_2\text{O}_7^{-2}$ ,  $\text{UO}_4^{-2}$ ,  $\text{MnO}_4^{-2}$ ,  $\text{Rh}^{+3}$ ,  $\text{Pt}^{+4}$ .

**Determination of bismuth.** The usual method for the colorimetric determination of small quantities of bismuth, which depends upon the use of an excess of potassium iodide to form the yellow coloration due to the  $\text{BiI}_4^-$  ion, cannot be satisfactorily carried out in the presence of lead, silver, copper and ferric ions. The yellow color produced by the addition of thiourea to a solution containing bismuth ions can, however, be used satisfactorily for this purpose.<sup>15,16</sup>

Ferric iron must be reduced by heating the solution with hydrazine sulfate.

Beer's law holds for the bismuth complex in the range 0.2-5 mg. of the metal per 100 ml. of solution.

**Procedure.** Evaporate the solution containing bismuth until nearly all the excess acid has been removed, and then dissolve the residue in water or nitric acid ( $d = 1.025$ - $1.030$ ) in such quantity as to make the resulting solution about 4-6 per cent in nitric acid. If iron is present, boil with a little hydrazine sulfate to reduce to the ferrous state, and then add 10-12 g. of thiourea with stirring for each 50 ml. of solution. Warm gently to dissolve, cool to  $15$ - $21^\circ \text{C}$ ., filter through a G4 filtering crucible, and wash the precipitate with 4-6 per cent nitric acid which is saturated with thiourea. Dilute the filtrate to a definite volume with 4-6 per cent nitric acid which is saturated with thiourea, and compare the color of this solution with that of standards containing known quantities of bismuth. The comparison is best made in a colorimeter.

The solution becomes turbid due to the separation of sulfur, particularly in presence of lead and copper. This can be prevented by the addition of hydrazine sulfate and keeping the mixture cool.

The concentration of the nitric acid must be great enough to prevent hydrolysis of the bismuth salt, but not so great as to have much effect upon the color.

Thiourea has been used for the determination of small quantities of bismuth in lead.<sup>17,18</sup>

**Procedure.** Boil 1 g. of the lead turnings with 10 ml. of nitric acid, add 5 ml. of water, cool, and add 10 ml. of 75 per cent tartaric acid. If a yellow color appears, add 3-5 drops of 3 per cent hydrogen peroxide and heat until the color disappears. Cool quickly and add 25 ml. of 75 per cent tartaric acid. Transfer to a 100-ml. volumetric flask, rinse the beaker with an 8 per cent thiourea solution, and then dilute to the mark with this solution. Measure the color with a Pulfrich photocolormeter, using a mercury lamp and Hg 436 filter. For 1 g. of sample the per cent Bi =  $0.42 E$  (extinction coefficient). This procedure is useful for 0.01-0.8 per cent bismuth.

**Determination of zinc.** Zinc can be determined as zinc quinaldate by precipitating with sodium quinaldate solution, but under ordinary conditions cobalt, silver and mercury interfere, since these ions also form insoluble precipitates. By means of thiourea, however, mercuric, silver, and cuprous ions can be converted into stable complexes and zinc can then be precipitated by

means of sodium quinaldate without interference.<sup>19,20</sup> The following procedure is recommended by Ray and Dutt<sup>20</sup> for the determination of zinc in the presence of copper, silver and mercury:

**Procedure.** Add about 8 g. (an excess) of potassium iodide to the solution to be analyzed, and treat the mixture with a freshly prepared solution containing 4-8 g. of sodium bisulfite. Add a solution of 4-8 g. of thiourea, 2-5 ml. of dilute acetic acid, and dilute the mixture to 200 ml. Heat, and to the hot solution add drop by drop an excess of 5 per cent neutral sodium quinaldate solution. Allow the precipitate to settle on a hot water-bath, wash thoroughly by decantation with hot water until a portion of the filtrate gives no test for an excess of sodium quinaldate with ferrous iron. Dry the precipitate at 125° C., and weigh as  $\text{Zn}(\text{C}_{10}\text{H}_6\text{NO}_2)_2 \cdot \text{H}_2\text{O}$ , which contains 15.29 per cent zinc.

**Detection and determination of cadmium.** Cadmium salts react with thiourea and Reinecke's salt,  $[\text{Cr}(\text{NH}_3)_2(\text{CNS})_4]\text{NH}_4$ , to form an insoluble compound, which can be used for the detection and determination of cadmium.

Mahr<sup>21,50</sup> has used the following method for the microchemical detection of cadmium:

**Procedure.** Evaporate 2 drops of the solution to be tested to dryness on a glass slide, and dissolve the residue in a small drop of 1-2 N hydrochloric acid. Mix with a large drop of a freshly prepared solution containing 1-1.5 per cent of Reinecke's salt and a drop of 5 per cent thiourea solution. The test depends upon the formation of crystals of  $\text{Cd}(\text{TH})_2[\text{Cr}(\text{NH}_3)_2(\text{CNS})_4]_2$ , where TH represents thiourea.

This test may be used in the presence of members of the third and fourth analytical groups. In the presence of cations of the second group, add to the original solution a hot mixture of concentrated ammonium hydroxide, hydroxylamine hydrochloride and sodium sulfite. Allow to stand for a time, filter, and test a drop of the ammoniacal solution with hydrochloric acid. Sometimes on heating, gold or platinum may precipitate at this point. Copper may be detected with the aid of a solution of Reinecke's salt; and, if a yellow precipitate of  $\text{Cu}[\text{Cr}(\text{NH}_3)_2(\text{CNS})_4]$  forms, treat the entire solution in the same manner, filter, and apply the cadmium test to the filtrate.

Mahr and Ohle<sup>22</sup> employ a procedure based upon the above reaction for the gravimetric determination of cadmium.

**Procedure.** Make the solution to be analyzed 0.1-1.0 N in mineral acid, and add a sufficient quantity of a filtered thiourea solution to make the concentration about 1 per cent. Then add a solution containing an excess of Reinecke's salt and 1 per cent thiourea. Allow to stand for 0.5-1.0 hours in ice water with occasional stirring, and filter off the pale red, finely crystalline precipitate through a glass filtering crucible. Wash with an ice cold 1 per cent thiourea solution, and then wash 3 or 4 times with cold alcohol. Dry at 110° C. and weigh. The precipitate corresponds to  $\text{Cd}(\text{TH})_2[\text{Cr}(\text{NH}_3)_2(\text{CNS})_4]_2$  and contains 12.47 per cent of cadmium.

Results obtained by this method are claimed to be excellent even in the presence of 1 per cent zinc. In the presence of other metals, more accurate results may be obtained by adjusting the acidity to approximately 0.1 N when making the precipitation.

The above procedure may be modified to a volumetric process by oxidizing the chromium in the precipitate to chromate and determining the latter by means of an iodometric titration.<sup>22</sup> Two methods are used to oxidize the chromium.

**Procedure.** *Oxidation with potassium bromate:* Precipitate the cadmium complex as described above, filter through a glass filter crucible, and wash as above with the thiourea solution. Transfer the crucible to a second suction flask, add a little pure potassium cyanide, and wash with hot water to dissolve everything on the filter. Add 1 ml. of hydrochloric acid, 0.5 ml. of a 1 per cent manganese sulfate solution, and sufficient sulfuric acid to make the acid concentration about 1 N (hood). Add 2 g. of potassium bromate and boil until bromine is no longer evolved. Filter off the precipitate of manganese dioxide, add 5 g. of ammonium sulfate, and boil until the excess bromate is removed. Cool, add an excess of potassium iodide, and titrate the liberated iodine with 0.1 N thiosulfate. 1 ml. 0.1 N thiosulfate = 1.8735 mg. cadmium.

*Oxidation with sodium peroxide:* Transfer the cadmium precipitate to a quantitative filter, wash with a 1 per cent thiourea solution, ash carefully and ignite gently in a nickel crucible until all organic matter is destroyed. Cool the residue and fuse with a little sodium peroxide. Place the crucible in a covered beaker, and dissolve the melt with a stream of hot water. Remove the crucible, wash, and boil the solution 15 minutes to destroy the excess peroxide. Add an excess of potassium iodide, acidify with 1:5 hydrochloric acid, and titrate the liberated iodine with 0.1 N thiosulfate.

A yellow precipitate of cadmium sulfide is formed when the cadmium ammonia complex is boiled with a solution of thiourea. This reaction has been used by Deniges<sup>23</sup> for the detection of cadmium.

**Procedure.** Add dilute ammonium hydroxide to 5 ml. of a solution containing cadmium until the precipitate which first forms redissolves, and then add 0.5-1.0 ml. of a 5 per cent solution of thiourea. A yellow precipitate of cadmium sulfide forms on boiling.

A somewhat similar reaction, proposed by Chalupny and Breisch,<sup>24</sup> is used for the separation of cadmium and zinc.

**Procedure.** Add a 33.3 per cent potassium cyanide solution to the cadmium-zinc mixture until a slight permanent precipitate is formed, and then add a sufficient excess to dissolve the precipitate and allow at least 4 g. of the potassium cyanide for each 1.0 g. of zinc. Add 10 ml. of a 4 N potassium hydroxide solution and heat to boiling. Just before the boiling point is reached, add 0.5-1.0 g. of thiourea for each 0.1 g. of cadmium, and boil the mixture for 30 minutes after the cadmium sulfide begins to precipitate. Filter immediately and wash the precipitate with water containing ammonium nitrate. Dissolve the cadmium sulfide in hot dilute hydrochloric acid, destroy the sulfide ion by

treating with a little hydrogen peroxide, and repeat the precipitation with thiourea. The final determination is carried out by dissolving the cadmium sulfide precipitate in a potassium cyanide solution and electrolyzing the mixture at 80° C. with a current of 5 amps. and 5 v.

Mahr<sup>25,26</sup> has used thiourea for the colorimetric determination of cadmium, copper and mercury. This method depends upon the quantitative precipitation of the metals as slightly soluble salts of Reinecke's acid,  $H[Cr(SCN)_4(NH_3)_2]$ , and thiourea. The cadmium complex consists of  $Cd(TH)_2[Cr(NH_3)_2(SCN)_4]_2$ , which contains the red ion,  $[Cr(SCN)_4(NH_3)_2]^-$ . This compound is soluble in organic ketones, and the red color of the resulting solution is suitable for colorimetric comparison. Methyl ethyl ketone is used as the solvent, since acetone is too volatile for satisfactory results.

**Procedure.** Precipitate the cadmium complex as described above.<sup>22</sup> Filter through a glass filter, wash and dissolve the moist precipitate by the addition of thiourea and methyl ethyl ketone containing 2 per cent thiourea. Dilute to a definite volume with the ketone and determine colorimetrically.

Copper and mercury are determined similarly. Precipitates of  $Cu(TH)_2[Cr(NH_3)_2(SCN)_4]_2$  and  $Hg(TH)_2[Cr(NH_3)_2(SCN)_4]_2$  are used.

**Detection and determination of lead.** A precipitate of  $2 Pb(NO_3)_2 \cdot 11CS(NH_2)_2$  is formed when a nitric acid solution of thiourea is added to a solution of a lead salt which has also been acidified with nitric acid. The formation of this precipitate can be used for the detection and the determination of lead.

Almost all other metals form soluble thiourea complexes or soluble nitrates and remain in solution. Aluminum, antimony, arsenic, barium, bismuth, cadmium, chromium, cobalt, copper, iron, manganese, mercury, nickel, silver and zinc do not interfere. Thallium, however, reacts like lead.

The following method for the microchemical detection of lead has been suggested by Mahr:<sup>27,49</sup>

**Procedure.** Make the solution to be tested about 1-2 N in nitric acid and evaporate a few drops to dryness on a glass slide. Moisten the perfectly dry residue with 1 drop of 2 N nitric acid and sprinkle a few particles of thiourea over it. As little as 0.02% of lead at a dilution of 1:40,000 can be detected by the formation of crystalline  $2Pb(NO_3)_2 \cdot 11CS(NH_2)_2$ .

The corresponding complexes of other ions are more soluble in dilute nitric acid and cause no interference with this procedure.

Mahr and Ohle<sup>78</sup> have used thiourea for the separation of lead from other metals, since only the lead complex with thiourea is insoluble in dilute nitric acid.

**Procedure.** Make the solution containing lead about 1-2 N in nitric acid, and add an equal volume of a saturated solution of thiourea in 1 N nitric acid. Cool the mixture to 0° C. in ice water, filter, and wash the residue with an ice cold 1-2 N nitric acid solution which is saturated with thiourea. Dis-

solve the washed precipitate in hot water and determine lead as the chromate, anthranilate, or picrolonate in the usual manner.

Lead is precipitated from solutions of alloys containing tin and antimony by the following procedure.

**Procedure.** Dissolve the alloy by treating with aqua regia and heating on a water-bath. Dilute the solution to 60-100 ml. and add 5-8 g. of solid thiourea. Lead precipitates on cooling.

If tartaric acid is necessary for complex formation, it is without effect upon the lead determination. If bismuth is present, the washed precipitate may be colored light yellow. In such cases, dissolve the precipitate in hot water, acidify with nitric acid, and reprecipitate with thiourea.

Lead peroxide may be determined by a reaction which is based upon its oxidizing properties. The peroxide is allowed to react with an excess of thiourea, and the excess is then measured by titration with a potassium bromate-potassium bromide solution in the presence of potassium iodide. For details of this procedure, see page 000.

**Determination of thallium.** Like lead, thallium forms with thiourea a precipitate corresponding to the formula  $\text{TlNO}_3 \cdot 4\text{TH}$ , in which TH represents thiourea. The lead perchlorate complex,  $\text{Pb}(\text{ClO}_4)_2 \cdot 6\text{TH}$ , is easily soluble in water, while the corresponding thallium salt,  $\text{TlClO}_4 \cdot 4\text{TH}$ , is very difficultly soluble. It is possible, therefore, to separate thallium from most other ions by means of thiourea in a solution containing perchloric acid.<sup>30</sup>

**Procedure.** Add perchloric acid to the solution to be analyzed until the concentration is about 2 per cent, and then add an equal volume of a 10 per cent thiourea solution. Allow to stand, while cooling with a stream of cold water, for about one-half hour. Filter, and wash the precipitate with a 5 per cent solution of thiourea containing a little perchloric acid. Dissolve the precipitate in hot water, make the solution acid with perchloric acid, and repeat the precipitation with thiourea. Thallium is finally determined as the chromate by adding potassium chromate and ammonia to the hot aqueous solution.

A somewhat more rapid procedure is based upon the following steps: Oxidize the thallium with bromine in presence of hydrochloric acid, remove the last traces of bromine with phenol, add potassium iodide and titrate the iodine which is formed by the oxidation of the iodide by thallic ions with sodium thiosulfate.

**Detection of germanium.** Thiourea has been used by Vanossi<sup>53,56</sup> to eliminate interference in the test for germanium with quinine tannate. For details of this test, see section on quinine (page 000).

**Detection and determination of osmium.** A rose to dark-red color is obtained when a solution containing osmium tetroxide or a chlorosmate is heated with thiourea and a little hydrochloric acid. This reaction is characteristic for osmium and has been used by Tschugaev<sup>81</sup> and others<sup>32-36,54</sup> for the detection of this element. The red compound appears to be  $[\text{Os} \cdot 6(\text{NH}_2\text{-CSNH}_2)]\text{Cl}_3 \cdot \text{H}_2\text{O}$ . The test of Tschugaev cannot be applied directly to solu-

tions containing large quantities of nitric acid, since under these conditions thiourea is decomposed. The test may be carried out, however, after previously destroying the nitric acid with sulfur dioxide. Gilchrist<sup>32</sup> states that this is one of the most delicate reactions for osmium, and is sensitive to 1 part of osmium in 5,000,000 parts of solution. For concentrations greater than 1:2,500,000, a pink color develops within less than 15 minutes.

Sandell<sup>52</sup> has used thiourea for the colorimetric determination of osmium. The sample solution should be strongly acid and free from oxidizing agents. When osmium is present as the tetroxide in 4 N hydrochloric acid solution, the color appears very soon after adding the thiourea, even at room temperature, and is fully developed within about 5 minutes. When osmium is present as the chlorosmate, however, the red color appears only slowly on boiling, but the development is more rapid in the presence of a little stannous chloride. Ruthenium gives a blue color with thiourea.

**Procedure.** To 10 ml. of a sample which is 4N in hydrochloric acid, and which contains not more than 10γ of osmium, add 0.50 ml. of 10 per cent aqueous thiourea solution. If osmium is present as the chlorosmate, also add 0.10 ml. of 10 per cent stannous chloride in 1:5 hydrochloric acid. Heat in a tube immersed in boiling water for 5 minutes if osmium is present as the tetroxide, or 10 minutes if present in the tetravalent state. Cool to room temperature and dilute to 25 ml. with water. A smaller total volume may be used. Determine the transmittancy, using a blue or green filter.

**Detection and determination of ruthenium.** A blue color is obtained when a solution of a ruthenium salt is heated for a short time with thiourea and hydrochloric acid. This reaction has been used for the detection of as little as 0.003 mg. of ruthenium per ml. of solution.<sup>34-37,53</sup>

Sandell<sup>55</sup> has also studied the use of thiourea for the colorimetric determination of small amounts of ruthenium. The hue and strength of the color formed in the reaction depend upon the acidity of the solution. In solutions in which the acidity ranges from 0.1 to 4 N in hydrochloric acid, the color varies from greenish to blue, and the intensity is greater with the higher acid concentrations. In 6 N hydrochloric acid, a violet color is obtained. The color may be developed in solutions ranging in acidity from 2 N to 4 N, although the latter seems preferable. The color develops rapidly on heating, and is fairly stable. Solutions containing 50γ of ruthenium in 10 ml. yield a slight turbidity on heating with thiourea, probably due to the slight solubility of the reaction product. A solution containing 25γ of ruthenium in the same volume remains clear. Ferric iron produces a turbidity due to the separation of sulfur.

**Procedure.** Adjust the acidity of the sample to 4 N in hydrochloric acid. To 10 ml. of this solution, containing up to 30-35γ of ruthenium, add 0.5 ml. of a 5 per cent aqueous solution of thiourea. Heat in a boiling water-bath for 10 minutes, and cool to room temperature. Dilute to 25 ml., or a smaller volume, and determine the transmittancy of the solution immediately, using a red filter.

**Detection of palladium.** Palladous salts in acid or ammoniacal solutions react with thiourea to form a yellow color. This reaction is sensitive to 5 p.p.m. of palladium.<sup>51</sup> Arreguine<sup>54</sup> has used thiourea for the microchemical detection of palladium. The test is more sensitive in the presence of inorganic anions. Hexagonal needles are obtained with chloride, bromide, or iodide, while triclinic yellow leaflets are formed in the presence of fluoride, sulfate, chromate, and phosphate. As little as 0.5 $\gamma$  of palladium can be detected in this way.

**Reactions of the platinum metals.** Whitmore and Schneider<sup>38</sup> have investigated the use of thiourea as a reagent for the microchemical detection of the platinum metals. The results obtained when a solid fragment of thiourea is added to 1 per cent solutions of the various platinum metal salts are given in Table 33.

TABLE 33.—REACTIONS OF THIOUREA WITH THE PLATINUM METALS

Test material	Description
RuCl <sub>3</sub>	A beautiful blue color develops
RhCl <sub>3</sub>	As the drop evaporates a few, small reddish-brown, hexagonal plates are formed near the circumference. Not a good test
PdCl <sub>2</sub>	Yellow crystals in the shape of halberd heads are formed, also rhomboids with cut off ends and radiates of slender prisms
Na <sub>2</sub> OsCl <sub>6</sub>	No apparent reaction
IrCl <sub>4</sub>	The test drop is decolorized. Some very small, colorless, rosette-like structures develop around the test particle
H <sub>2</sub> PtCl <sub>6</sub>	Some long reddish-brown mossy dendrites appear
AuCl <sub>3</sub>	A brown precipitate, which gradually becomes dark and finally black forms around the test particle. Sometimes a few colorless hexagonal plates are formed

**Detection of selenium.** Thiourea is an excellent reducing agent for selenium. It instantly liberates selenium as a red powder from hydrochloric acid solutions of selenium compounds, even when only traces of the element are present. This reaction is capable of detecting 5 p.p.m. of selenite ion.<sup>51</sup> No other reducing agent is satisfactory in the presence of hydrochloric acid and many other ions. Falcicola<sup>39</sup> has made this reaction the basis for a spot test for selenium.

**Procedure.** Impregnate filter paper with a solution of thiourea and moisten with a drop of the solution to be tested which has been acidified with hydrochloric acid. An orange-red spot is formed if selenium is present.

Copper may interfere by forming an insoluble compound. Nitrates must be absent, but the separation is easily effected by extracting with ethyl acetate or ether.

Selenites may be detected by the following procedures proposed by Deniges:<sup>40</sup>

**Procedure.** Place a little of the solid sample in a porcelain dish, and add a drop of a 5 per cent aqueous solution of thiourea. Mix well and add 1 drop



of 1 N hydrochloric acid. A red precipitate of selenium appears immediately if selenites are present. Under the same conditions selenates yield a precipitate only after several minutes.

This reaction may be used for the detection of selenium in commercial sulfuric acid and in natural waters. The following procedure is used for detecting selenium in water:

**Procedure.** Evaporate a 60-ml. sample of the water to be tested to 4 ml., and add 5 drops of hydrochloric acid. Transfer to a small graduated cylinder and dilute to 6 ml. with water. Mix well and filter. To 5 ml. of the clear filtrate, add 2 drops of hydrochloric acid and 5 drops of a 5 per cent aqueous solution of thiourea. Boil and allow to cool for 5 minutes. A turbidity is produced with as little as 0.05 mg. of selenium.

If the water to be analyzed contains sodium bicarbonate, make just acid with hydrochloric acid.

Evans <sup>41</sup> has used thiourea for the microchemical detection of selenium:

**Procedure.** Add 1 drop of 10 per cent thiourea to 1 drop of the material to be tested in cold 1:5 hydrochloric acid. An amorphous red precipitate forms if selenium is present. The reaction is sensitive to 0.01 per cent selenium.

Copper and mercury must be removed before making the test.

**Detection of tellurium.** Unlike selenium, tellurium is not formed when thiourea is added to solutions of tellurium salts. This is true of dilute and concentrated acid solutions and neutral solutions. When the solution is concentrated, a yellow crystalline precipitate is formed which is insoluble in ordinary organic solvents except ethyl alcohol. This reaction is very sensitive, a yellow color appearing with as little as 1 part of tellurium in 500,000 parts of solution. This reaction may be carried out on filter paper, although bismuth and antimony give similar colors.<sup>42</sup>

**Detection of ferricyanide.** Storfer <sup>43</sup> has used thiourea in a spot test for ferricyanides. As little as 0.4γ of ferricyanide at a dilution of 1:100,000 can be detected by the formation of the red-violet compound,  $[\text{CuTH}_3]_3\text{Fe}(\text{CN})_6 \cdot 2\text{H}_2\text{O}$ , in which the Cu is univalent and TH represents 1 mole of thiourea.

**Reagent.** Add slowly 3 moles of cupric chloride to an aqueous solution containing 1 mole of thiourea heated to 70° C. Recrystallize the product from warm (not hot) water. Impregnate filter paper with a solution saturated with this compound at 70° C., and dry in vacuum.<sup>44</sup>

**Procedure.** Add a drop of the neutral solution to be tested to the reagent paper. A red or gray-violet spot is obtained if ferricyanide is present.

**Determination of oxidizing agents.** The oxidation of thiourea to the disulfide,  $[\text{NH}_2(\text{NH})\text{CS}]_2$ , may be used for the determination of chromates, chlorates, bromates, manganese dioxide, lead peroxide and many per-compounds.

The oxidant is allowed to act upon an excess of thiourea, and the excess is measured by titration with potassium bromate-potassium bromide in the presence of potassium iodide.<sup>45-47</sup>

The following procedure is used for the determination of chlorates.

**Procedure.** Mix 20 ml. of 18 N sulfuric acid, 5 ml. of 1 per cent potassium iodide solution, and a carefully measured volume of 0.1 N thiourea solution. Carefully rotate the contents of the flask and add the chlorate solution to be analyzed. Heat at 70° C. for 10-15 minutes, cool to 35° C., and add a little starch indicator solution. Dilute to about 80 ml., and titrate with a 0.1 N potassium bromate-potassium bromide solution, or with a 0.1 N solution of potassium permanganate. Titrate to the appearance of a blue color, then dilute with warm water (35° C.) to 250-300 ml., and titrate to a change to a light blue color. One ml. of 0.1 N thiourea solution = 2.0425 mg. of KClO<sub>3</sub>. Results obtained in a number of determinations using this method are given in Table 34.

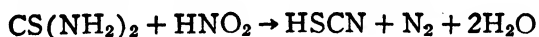
TABLE 34.—DETERMINATION OF POTASSIUM CHLORATE

KClO <sub>3</sub> Used mg.	KClO <sub>3</sub> Found mg.	0.1N Thiourea Added ml.	Back Titration 0.1N KBrO <sub>3</sub> —KBr or 0.1N KMnO <sub>4</sub> Used ml.
26.42	26.53	20	7.01
26.42	26.41	20	7.07
27.79	27.70	20	6.44
27.79	27.68	20	6.45
52.84	52.48	30	4.33
52.84	52.85	30	4.13
55.15	55.34	30	2.91
55.15	55.01	30	3.07

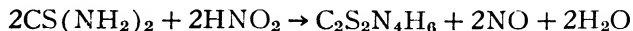
Employ the same procedure for determining bromates, and add the bromate solution very slowly. Heating on a water-bath is unnecessary, but the solution should be heated to 35° C. before titrating. Results claimed for this method agree within 0.03 ml. of 0.1 N solution.

Chromates can be titrated directly with a thiourea solution, using a starch-potassium iodide solution as the indicator. Titration of chromates with thiourea can be carried out quantitatively by adding a small amount of potassium iodide and starch to the chromate solution. The oxidation of thiourea to the disulfide is thereby accelerated, and the end-point of the reaction is shown by the disappearance of the iodine-starch color. Molybdenum, vanadium, tungsten, copper and iron do not interfere.

**Determination of nitrites.** Thiourea and nitrous acid react in the presence of acetic acid according to the following equation:



In the presence of a strong acid, such as hydrochloric acid, the reaction takes place somewhat differently:



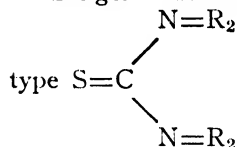
It will be observed, however, that in the above reactions, whether as nitrogen or as nitric oxide, the volume of the gas evolved in both reactions is the same. Coade and Werner<sup>29</sup> have used these reactions for the gasometric determination of nitrites. These authors claim that the method is more satisfactory than that with urea, since it is more rapid and clearer.

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**Substituted thioureas.** Yoe and Overholser<sup>1</sup> have studied a number of substituted thioureas as analytical reagents. These react in much the same manner as thiourea, and seem to offer no advantages over the parent substance.

Steiger<sup>2</sup> has studied the reactions of a number of thiourea derivatives of the



in which R = H alkyl radical, aryl radical or NHR. Many of these compounds ruthenium to form colors ranging from red to blue, and some react with osmium to give green colors. A summary of these reactions is given in Table 35.

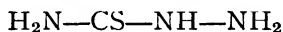
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## THIOSEMICARBAZIDE

$\text{CH}_5\text{N}_3\text{S}$

Mol. Wt. 91.13

Beil. Ref. III, 195



**Use:** Determination of chromium.

Thiosemicarbazide is obtained as a white crystalline solid from water. It melts at 182-184° C. It is soluble in water and in alcohol.

**Procedure.** Warm 50 g. of hydrazine sulfate with 20 ml. of water and 27 g. of anhydrous potassium carbonate, and add 40 g. of potassium thiocyanate. Boil for a few minutes and mix with 200-300 ml. of hot alcohol. Filter with suction, free the filtrate from alcohol, and then boil with vigorous shaking until blisters begin to form on the surface of the syrupy mass. Cool and mix

TABLE 35.—REACTIONS OF SUBSTITUTED THIOUREAS WITH RUTHENIUM

Compound	Color of Product	Limit of Detection $\gamma$ Ru./ml.	Reaction with Osmium <sub>2</sub>	Remarks
$H_2N-CS-NHCH_3$	Blue	0.08	No reaction	{ Ruthenium compound { extracted with ether
$H_2N-CS-NHC_6H_5$	Blue	0.08	No reaction	
$(CH_3)_2N-CS-NHCH_3$	Red	0.13		{ Ruthenium compound { extracted with ether
$(CH_3)_2N-CS-N(CH_3)_2$	Violet	0.13		
$H_2N-CS-NHNH_2$	Red $\rightarrow$ green	0.14	No reaction	{ Ruthenium compound { extracted with ether
$H_2N-CS-NHNHC_6H_5$	Violet	....	Green color	
$C_6H_5NH-CS-NHNHC_6H_5$	Violet	0.025 *	Green color	{ Ruthenium compound { extracted with ether
$C_6H_5NH-CS-N(NH_2)C_6H_5$	Violet	0.017		
$C_6H_5NH-C(SH)=N-NHC_6H_5$	Violet	0.025	Green color	{ Ruthenium compound { extracted with ether
$H_2NNH-CS-NHNH_2$	Red	0.6		
$C_6H_5NNH-CS-NHNHC_6H_5$	Violet	....	Green color	

with water and filter with suction. Again evaporate the filtrate to obtain an addition quantity of the reagent. Recrystallize from water.<sup>1</sup>

**Determination of chromium.** Hanus and Lukas<sup>2</sup> have used thiosemicarbazide for the gravimetric determination of chromium. Chromium hydroxide is precipitated quantitatively from a neutral or alkaline solution of a chromate by means of hydrazine hydrate and some of its derivatives, such as hydrazine sulfate, phenylhydrazine and thiosemicarbazide. The latter appears to be the most satisfactory. The addition of a salt such as ammonium chloride makes the precipitation more rapid and quantitative. For the separation of chromium from aluminum and iron, treat with ammonium hydroxide and hydrogen peroxide, and then precipitate chromium in the filtrate with thiosemicarbazide. Satisfactory results are reported using this method.

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### TOLUENE-3,4-DITHIOL

Synonym: 4-Methyl-1,2-dimercaptobenzene, dithiol

$C_7H_8S_2$

Mol. Wt. 156.25

$CH_3-C_6H_3(SH)_2$

**Use:** Detection of bismuth, molybdenum, rhenium, tin, and tungsten.

**Determination of tin.**

Toluene-3,4-dithiol is a low-melting solid, which is transformed to a colorless oil at 31° C. It boils at 185-187° C. at 84 mm. pressure.

**Preparation:** Reflux 14.8 g. of powdered sodium toluene-3,4-disulfonate for 4 hours with 21 g. of phosphorous pentachloride and 10 ml. of phosphorus oxychloride. Pour the mixture onto ice, and recrystallize the solid product from a light petroleum fraction (B.P. = 80-100° C.). Reduce 45 g. of the above compound by boiling with 350 g. of tin and 1000 ml. of concentrated hydrochloric acid for 20 minutes. Then rapidly cool the flask and its contents, and add 150 ml. of benzene. Filter immediately at 40° C., and extract the aqueous layer with benzene. Combine the benzene extracts and dry over sodium sulfate. Remove the benzene by distillation, and distill the residual oil *in vacuo*. Retain the fraction coming over at 185-87°/84 mm.<sup>1</sup>

**Detection of tin.** Toluene-3,4-dithiol, like 4-chlorobenzene-1,2-dithiol, reacts with solutions of stannous salts to give a pink or red precipitate which can be used for the detection of tin.<sup>2-5</sup> The test is carried out as follows:

**Reagent.** Dissolve 0.2 g. of toluene-3,4-dithiol, in 100 ml. of 1 per cent sodium hydroxide solution.

**Procedure.** Add a few drops of the reagent to an acid solution (which may contain up to 15 per cent hydrochloric acid) containing tin. A pink-red

color is produced when only 1 part of tin is present in 1,000,000 parts of solution. The red color develops very rapidly if the tin is present in the form of stannous salts, but the reaction occurs more slowly with stannic salts. The test can be made more rapidly by the addition of a little thioglycolic acid to reduce the stannic ion.

Many cations react with the reagent to yield colored compounds which may interfere with the tin test. Only bismuth, however, yields a red compound, although the color of the other compounds may mask that caused by the reaction with tin. The interference with his test is the same as that described above with the 4-chlorobenzene-1,2-dithiol.

**Determination of tin.** Clark<sup>2</sup> recommends the use of toluene-3,4-dithiol in preference to ~~the~~ 4-chloro-derivative for the colorimetric determination of tin, because of the greater ease with which the former can be prepared. Further, there is no necessity for keeping the reagent stored in an atmosphere of hydrogen to prevent oxidation, and this eliminates a somewhat troublesome procedure when the 4-chloro-compound is used.

According to Clark, the comparison of the unknown and standard suspensions must be made by reflected light. If the tin concentration of the solution does not exceed 30 p.p.m., a protective colloid such as agar is not necessary. Magnesium, aluminum, zinc, the alkali and alkaline earth metals, halides, thiocyanate, cyanide, borate, oxalate and tartrate do not interfere in concentrations below 2 per cent. Phosphate decreases the color intensity, and fluoride delays the color development. Iron may be present in concentrations up to 0.5 per cent, and manganese up to 1 per cent. Lead gives no color if the hydrochloric acid concentration is 7 per cent. Nitrites cause a red color.

**Reagent.** Dissolve 0.2 g. of toluene-3,4-dithiol in 100 ml. of 1 per cent sodium hydroxide solution, and add 0.3-0.5 g. of thioglycolic acid.

The reagent is easily oxidized and cannot be kept indefinitely, but the addition of thioglycolic acid increases its stability. The reagent should be prepared at least every two weeks.

**Procedure.** Treat the acid solution to be analyzed with dilute thioglycolic acid (2-3 drops per liter) to ensure the reduction of any stannic tin to the stannous condition, and dilute the solution until the concentration does not exceed 60 p.p.m. of tin. Place a 5-ml. aliquot of this solution in a graduated test tube, and add 1 ml. of concentrated hydrochloric acid, and then treat with 1 ml. of agar jelly, which prevents the coagulation of the red tin precipitate and permits a colorimetric comparison. Boil until all the agar is in solution and cool under the tap, and then add 2 ml. of the toluene-3,4-dithiol reagent. Dilute to 10 ml., and heat in boiling water for one minute. Measure the color in a Lovibond tintometer. The amount of tin is obtained from measurements previously made with standards containing known quantities of tin.

The comparison may be made by a series of standards method. Compare by examining the color from the side in reflected light.

**Detection of molybdenum, tungsten and rhenium.** A green precipitate is obtained with molybdenum under the conditions described above in the test for tin. When thioglycolic acid and toluene-3,4-dithiol are added to solutions of metal salts in dilute hydrochloric acid, and the resulting complex is treated with concentrated ammonium hydroxide, all the precipitates dissolve to form nearly colorless solutions except that with molybdenum, which produces a brilliant blue solution. This reaction constitutes an excellent test for molybdenum. Pentavalent rhenium also forms a green complex, and tungsten yields a light greenish-blue precipitate.<sup>5-8</sup> To detect either molybdenum or tungsten alone in a solution, use the following procedure:

**Reagent.** Dissolve 0.2 g. of toluene-3,4-dithiol in 100 ml. of 1 per cent sodium hydroxide solution and add 0.3-0.5 g. of thioglycolic acid.

**Procedure.** To 10 ml. of a solution containing 0.02-1.0 mg. of either tungsten or molybdenum, add sodium hydroxide or hydrochloric acid, whichever is required, until the mixture is neutral to litmus. Then add 10 drops of concentrated hydrochloric acid and 3 drops of thioglycolic acid. If molybdenum is present, a bright yellow precipitate forms at this point. Tungsten gives no color. Next add 1 ml. of the toluene-3,4-dithiol reagent. A dark green precipitate forms with molybdenum, and a light greenish-blue precipitate appears if tungsten is present. Cool the mixture and add an excess of concentrated ammonium hydroxide. A bright blue color is formed if molybdenum is present, but with tungsten there is no color. By means of this reaction 0.02 mg. of molybdenum can be detected in 10 ml. of solution.

The following procedure is used to detect tungsten in the presence of molybdenum:

**Procedure.** Make 20 ml. of a solution containing 10 mg. of molybdenum and 0.1 mg. of tungsten basic to litmus with sodium hydroxide, and add 2 g. of tartaric acid and 0.2 ml. of concentrated sulfuric acid. Heat the mixture to 60° C. and saturate with hydrogen sulfide. Filter off the precipitate of molybdenum sulfide, evaporate the filtrate to dryness, and ignite to destroy the tartaric acid. Add a few drops of 20 per cent sodium hydroxide solution to the residue, dilute the mixture with water, and then test for tungsten by the procedure described above.

Heptavalent rhenium reacts with toluene-3,4-dithiol to form a green complex similar to that of molybdenum, but unlike the latter, the rhenium complex is decomposed by potassium thiocyanate. The addition of 1 drop of a 1 per cent solution of toluene-3,4-dithiol in 1.0 N sodium hydroxide to 1 ml. of a hydrochloric acid solution containing 5γ of rhenium (as the perrhenate) produces no color in a cold solution if the acid concentration is less than 2 N, but a pale green color appears in 11 N acid. A pale green color develops in the 2 N acid solution if the mixture is heated for 5 minutes. Under the same conditions 5γ of hexavalent molybdenum gives a green color in the cold acid solutions ranging from 0.5 N to 11 N. Heating has only the effect of developing



the color slightly. Hexavalent tungsten gives no color in the cold, and a blue-green color develops only in a 0.5 N acid solution.

The complexes of rhenium, tungsten and molybdenum are readily soluble in normal butyl acetate and chloroform. When orange-red solutions of  $\text{Mo}(\text{OH})_2(\text{SCN})_3$  or orange yellow  $\text{ReO}(\text{SCN})_4$  in normal butyl acetate are heated with hydrochloric acid and a little toluene-3,4-dithiol, the green molybdenum complex is formed at once in the presence of concentrated acid, and after a short time if the acid is more dilute. The rhenium compound, on the other hand, gives only a color change from orange-yellow to reddish-brown. When solutions of the green complexes of molybdenum, rhenium and tungsten with toluene-3,4-dithiol are dissolved in normal butyl acetate, and are then treated with hydrochloric acid and potassium thiocyanate, the solution of the rhenium compound changes to a red-brown, while those of molybdenum and tungsten are unchanged. By means of this reaction, rhenium can be differentiated from molybdenum.<sup>2</sup>

Miller and Lowe<sup>5</sup> have used toluene-3,4-dithiol as a confirmatory test for tungsten in a systematic scheme of analysis. The test is carried out as follows:

**Procedure.** To 1 ml. of a solution of a tungstate in 2 N sodium hydroxide, add an excess of a freshly prepared 1 per cent solution of toluene-3,4-dithiol in 0.5 N sodium hydroxide. Add 2-4 N phosphoric acid dropwise and with constant shaking until a turbidity just appears. If tungsten is absent, or present only in very small quantities, the turbidity is white, but with considerable quantities of tungsten, a violet turbidity is formed. With further small additions of phosphoric acid, a buff then a blue-green suspension is formed. After the turbidity appears, allow the mixture to stand for a short time for the color to develop, and then add another drop of acid. When no further change occurs, heat the mixture in boiling water for several minutes and extract the green complex with butyl acetate. By this method 5γ of tungsten can be detected.

Tungsten can be determined colorimetrically by a procedure similar to that described above by extracting the colored complex with butyl acetate and comparing the color of the resulting solution with that of standards containing known quantities of tungsten. The concentration of the tungsten should not exceed 40γ per ml. of the solvent. If phosphoric acid is replaced by hydrochloric acid, a more careful control of the addition of the acid is required. Molybdenum and vanadium interfere with this determination.

Miller<sup>9</sup> has also used isoamyl acetate to extract the bluish-green complex of tungsten and toluene-3,4-dithiol.

**Detection of bismuth.** Miller and Lowe<sup>5</sup> have used toluene-3,4-dithiol as a confirmatory test for bismuth in a systematic scheme of analysis. Bismuth forms a brick-red complex with a freshly prepared 0.2 per cent solution of toluene-3,4-dithiol in 0.25 N sodium hydroxide. With this reagent, as little as 10γ of bismuth can be detected in 0.5 ml. of solution. Tin gives a red color with the reagent, but this interference may be eliminated by the addition of hydrogen fluoride, which does not influence the test. Tellurites interfere by

giving a buff precipitate with the reagent and depositing elementary tellurium on heating. Antimony does not interfere with concentrations less than 5 times that of the bismuth.

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3. R. E. D. Clark, *Tech. Pub. Intern. Tin Research Development Council Ser. A.* **41**, 7 pp. (1936); *C.A.* **30**, 6302 (1936).
4. R. E. D. Clark, *Analyst.* **61**, 242-45 (1936); *C.A.* **30**, 3741 (1936).
5. C. C. Miller and A. J. Lowe, *J. Chem. Soc.* 1258-63 (1940); *C.A.* **35**, 707-8 (1941).
6. J. H. Hamence, *Analyst.* **65**, 152-54 (1940); *C.A.* **34**, 2729 (1940).
7. C. C. Miller, *J. Chem. Soc.* 792 (1941); *C.A.* **36**, 2228 (1942).
8. C. C. Miller, *J. Chem. Soc.* 72-4 (1943); *C.A.* **37**, 3690 (1943).
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## CHAPTER VI

### SULFONIC ACIDS

The sulfonic acid group generally has little effect upon the analytical properties of an organic molecule, except to increase its solubility. Some sulfonic acids, however, have been used as precipitants for potassium and the alkaline earths, and also as alkalimetric standards. A great many compounds used in analytical procedures contain one or more sulfonic acid groups, but the greater number of these contain also other functional groups which are responsible for their analytical properties. A number of sulfonic acids not elsewhere listed are included in this section.

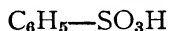
#### BENZENEMONOSULFONIC ACID

Synonym: Phenylsulfonic acid, benzenesulfonic acid



Mol. Wt. 176.19

Beil. Ref. XI, 26



**Use:** Detection of ammonium and potassium.

Determination of zinc.

Benzenemonosulfonic acid consists of white or almost white, very hygroscopic tabular crystals. It melts at 43-44°, or 50-51° C. when anhydrous. It is quite soluble in water and alcohol, but is only slightly soluble in benzene, and is insoluble in ether and carbon disulfide.

**Preparation:** Mix 60 ml. of benzene and 60 ml. of concentrated sulfuric acid in a 500-ml. flask equipped with a vertical condenser, and heat on a sand-bath with frequent shaking for about 6-8 hours, or until the upper layer of benzene has almost disappeared. Cool, and pour the dark colored liquid into a liter of cold water. Boil, and neutralize the mixture with powdered chalk. Filter hot through a porcelain funnel, and concentrate the filtrate somewhat. Then treat with just sufficient sodium carbonate solution to precipitate the calcium as calcium carbonate, and convert the sulfonic acid to the sodium salt. Again filter through a porcelain funnel and concentrate the solution by first heating over a free flame and finally on a water-bath until a sample crystallizes on cooling. Drain with suction and dry on a porous plate.<sup>1,2</sup>

**Detection of ammonium and potassium.** Rosenthaler<sup>3</sup> has investigated the use of benzenemonosulfonic acid as a microchemical reagent for ammonium and potassium salts, but has found that characteristic microcrystals are not formed with this reagent.

**Determination of zinc.** The precipitation of zinc as zinc sulfide presents some difficulty in analytical procedures due to the difficulty in obtaining a

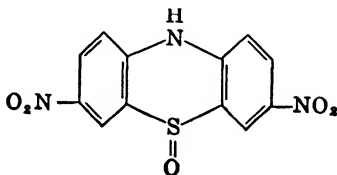
filterable precipitate. Schilling<sup>4</sup> has recommended the use of benzenemonosulfonic acid to render the zinc sulfide precipitate granular and permit a rapid filtration and washing.

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2. A. Michael and A. Adair, *Ber.* **10**, 585 (1877).
3. L. Rosenthaler, *Mikrochemie.* **2**, 29-32 (1924); *C.A.* **18**, 2481 (1924).
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## DINITRODIPHENYLAMINESULFOXIDE

$C_{12}H_7O_5N_3S$

Mol. Wt. 305.24 Beil. Ref. XXVII, 67 (229)



**Use:** Determination of tin.

Dinitrodiphenylaminesulfoxide occurs as yellowish-red needles or prisms. It decomposes on heating. It is insoluble in all ordinary solvents, but dissolves in ammonia and alkalis with the formation of bluish-red solutions.

**Preparation:** Cool 20 parts of nitric acid ( $d. = 1.44$ ) with ice, and add slowly in very small quantities 1 part of thioldiphenylamine, keeping the temperature below  $5^{\circ} C$ . Allow to stand 4-5 hours and filter the resulting nitro compound on asbestos. Wash with strong nitric acid ( $d = 1.44$ ), and then with more dilute acid, and finally with pure water. Extract with hot alcohol, in which the compound is not appreciably soluble. The resulting product is almost pure.<sup>1</sup>

**Determination of tin.** Dinitrodiphenylaminesulfoxide is reduced with stannous chloride in the presence of hydrochloric acid to form the corresponding 2,7-diamino compound. This reaction is used for the colorimetric determination of tin.<sup>1</sup> Tin is determined in food products as follows.

**Procedure.** Place 50 g. of the material to be analyzed in a round-bottomed flask, together with 50 g. of potassium bisulfate and 50 ml. of concentrated sulfuric acid. Add more sulfuric acid if necessary to keep the mixture fluid. After the solution has become colorless, cool, dilute with water to about 600 ml., treat with hydrogen sulfide, and allow to stand overnight. Filter, wash a few times with water, and transfer the filter and contents to a large test tube. Add 5 ml. of concentrated hydrochloric acid and boil, and filter through a small funnel, and then wash the residue with 2.5 ml. of hydrochloric acid. Close the test tube with a cork carrying a tube through which carbon dioxide is passed. While still hot, add a small piece of zinc foil, and when all of the metal has dissolved, add 2 ml. of a reagent prepared by dissolving 0.2 g. of dinitrodiphenylaminesulfoxide in 100 ml. of 0.1 N sodium hydroxide and filtering. Continue the addition of carbon dioxide. Boil the mixture a few minutes, dilute

to 100 ml. with cold water, filter, and treat the filtrate with a drop of ferric chloride solution. Finally compare the violet coloration which is thus produced with that formed by standards containing known quantities of tin.

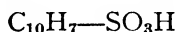
1. G. S. Buchanan and S. B. Schryver, *British Food Journal*. 11, 101 (1908); *C.A.* 3, 2329 (1909).

### NAPHTHALENE- $\alpha$ -SULFONIC ACID



Mol. Wt. 244.26

Beil. Ref. XI, 155



**Use:** Detection of ammonium, magnesium and potassium.

Determination of potassium,

Naphthalene- $\alpha$ -sulfonic acid is a white crystalline solid which melts at 90° C. It is freely soluble in water and alcohol, but is only slightly soluble in ether.

**Preparation:** Place 260 g. of sulfuric acid monohydrate in a beaker and cool to 0° C. While stirring mechanically, add quickly 128 g. of finely powdered naphthalene. When well mixed inoculate the mass with a little naphthalene- $\alpha$ -sulfonic acid and allow to stand for about one hour, during which naphthalene- $\alpha$ -sulfonic acid separates as a crystalline mass. The temperature should not rise above 30° C. during the reaction period. Dilute the mixture with 1.15 liters of water and allow the mixture to stand overnight. Filter and evaporate the clear colorless solution at 20 mm. pressure at 35° C. to a sp. gr. of 1.29-1.30. Place the mixture in a refrigerator for a few days until the mass has solidified as the dihydrate of naphthalene- $\alpha$ -sulfonic acid. It may be necessary to inoculate the syrupy mixture before crystallization takes place. Break up the mass and filter off the excess liquid through cotton. Press out the residual liquid and dissolve the residue in one-tenth of its weight of hot water. Then add 30-35 per cent hydrochloric acid until the hydrochloric acid content is 20 per cent, and again allow to stand for 24 hours in a refrigerator. All the excess sulfuric acid is removed by repeating the precipitation 3 or 4 times.<sup>1,2</sup>

**Detection of ammonium, magnesium and potassium.** Rosenthaler<sup>3</sup> has used a saturated aqueous solution of sodium  $\alpha$ -naphthalenesulfonate for the microchemical detection of potassium, ammonium and magnesium ions. With these ions the reagent gives characteristic crystals. Manganese, zinc, barium, strontium, and calcium must be absent.

**Determination of potassium.** Winkel and Maas<sup>4</sup> have used naphthalene- $\alpha$ -sulfonic acid in a procedure for the rapid determination of potassium. The determination includes the following steps: Precipitate potassium in the usual manner with dipicrylamine, dissolve the precipitate in acetone, dilute the solution with water until the acetone content is 20-30 per cent, and then titrate conductometrically with a 0.1 N solution of hydrochloric acid or naphthalene- $\alpha$ -sulfonic acid.

1. M. Merz and W. Weith, *Ber.* **3**, 195, 196 (1870).
2. H. E. Fierz and P. Weissenbach, *Helv. Chim. Acta.* **3**, 315 (1920).
3. L. Rosenthaler, *Mikrochemie.* **2**, 29-32 (1924); *C.A.* **18**, 2481 (1924).
4. A. Winkel and H. Maas, *Angew. Chem.* **49**, 827-30 (1936); *C.A.* **31**, 627 (1937).

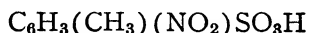
***p*-NITROTOLUENESULFONIC ACID**

Synonym: 4-Nitrotoluene-2-sulfonic acid



Mol. Wt. 253.23

Beil. Ref. XI, 90



**Use:** Alkalimetric standard.

*p*-Nitrotoluenesulfonic acid crystallizes from water with 2 molecules of water of hydration. It melts at 133.5° C. The anhydrous compound is formed at 130° C. The compound is soluble in water, alcohol, ether and chloroform.

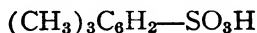
**Preparation:** Add 50 g. of *p*-nitrotoluene to 200 g. of fuming sulfuric acid and heat the mixture for a short time on a water-bath to complete sulfonation. Pour the mixture into 300 ml. of water and allow to cool. Filter with suction and recrystallize from hot water. To a saturated solution of the reagent add an equal volume of concentrated hydrochloric acid. Repeat the precipitation with hydrochloric acid 3 times to free the crystals from sulfuric acid, and finally recrystallize several times from pure water.<sup>1</sup>

**Use as alkalimetric standard.** Kastle<sup>2</sup> has proposed the use of *p*-nitrotoluenesulfonic acid as a standard in alkalimetry. The compound is stable in air under ordinary conditions. It is not hygroscopic and not deliquescent, and gives a sharp end-point with phenolphthalein. It is easily prepared and readily obtained in a pure state. The use of this standard is sufficiently accurate for all practical purposes.

1. J. H. Kastle, *Am. Chem. J.* **44**, 483-7 (1910).
2. J. H. Kastle, *Am. Chem. J.* **44**, 487-93 (1910); *C.A.* **5**, 846 (1911).

**PSEUDOCUMENESULFONIC ACID**

Mol. Wt. 236.28



**Use:** Standard in alkalimetry.

Pseudocumenesulfonic acid is obtained as glistening plates containing 1.5 moles of water of hydration. It melts at 111-112° C. (anhydrous, 128-131° C.).

**Preparation:** Mix 100 ml. of pseudocumene with 200 ml. of concentrated sulfuric acid in a flask fitted with a short air condenser. Allow to stand until solution is complete, then cool the mixture, and pour with constant and vigorous stirring into 400 ml. of concentrated hydrochloric acid kept at 10° C. or lower, or pour onto 300 g. of ice. Filter with suction through a cloth filter, and press as dry as possible. Recrystallize from 20 per cent hydrochloric acid.<sup>1</sup>

**Standard in alkalimetry.** Pseudocumenesulfonic acid is a strong acid and can be used as an alkalimetric standard with most indicators. It crystallizes with 2 moles of water of hydration, and the dihydrate has a very low vapor pressure.

1. L. I. Smith and O. W. Cass, *J. Am. Chem. Soc.* **54**, 1606 (1932).
2. D. Tishchenko, *Bull. soc. chim.* **53**, 1423-8 (1933); *C.A.* **28**, 3332 (1934).

### SODIUM ANTHRAQUINONE-2,7-DISULFONATE

$C_{14}H_6O_8S_2Na_2 \cdot 4H_2O$

Mol. Wt. 368.32

Beil. Ref. XI, 342



**Use:** Determination of gaseous hydrogen.

**Preparation:** Sodium anthraquinone-2,7-disulfonate is prepared by sulfonating anthraquinone with fuming sulfuric acid. Use 110 per cent of theory of fuming sulfuric acid containing 40 per cent  $SO_3$ , and carry out the sulfonation at  $190^\circ C$ . The product consists of a mixture of 2,6- and 2,7-anthraquinone disulfonic acid in the ratio 1:1.15. It is difficult to separate the pure compound, but this is unnecessary when the reagent is used for the determination of hydrogen.<sup>1</sup>

**Determination of hydrogen.** An aqueous solution of sodium anthraquinone-2,7-disulfonate and colloidal palladium, peptized by an alkaline solution of sodium protalbinat, is recommended by Bonney and Huff<sup>2</sup> for the absorption of hydrogen from gaseous mixtures. This reagent has the advantage of being readily revived by contact with oxygen or air, and at ordinary temperatures absorbs about 15 ml. of hydrogen per minute. Hydrogen can be determined with the use of this reagent when nitrogen and saturated hydrocarbons are present, but carbon dioxide, unsaturated compounds, oxygen, and carbon monoxide should be removed. Hydrogen and oxygen can be determined simultaneously. The reagent is rendered inactive by contact with carbon monoxide and carbon disulfide, but it soon regains its activity after standing in air or oxygen.

1. K. Lauer, *J. prakt. Chem.* **130**, 185 (1931); *C.A.* **25**, 4259 (1931).
2. D. T. Bonney and W. J. Huff, *Ind. Eng. Chem., Anal. Ed.* **9**, 157-62 (1937); *C.A.* **31**, 3819 (1937).

## CHAPTER VII

### THE SULFINIC ACIDS

The water-soluble benzenesulfinic acid,  $\text{C}_6\text{H}_5\text{—SO}_2\text{H}$ , and its alkali salts react with ferric salts, even in solutions of mineral acids, to form the slightly soluble, orange-yellow ferric benzenesulfinate,  $(\text{C}_6\text{H}_5\text{—SO}_2)_3\text{Fe}$ .<sup>1</sup> This compound is so insoluble that it is formed in solutions containing fluoride and phosphate ions, which greatly reduce the ferric ion concentration by forming complex ions. Further, a distinct turbidity appears when benzene sulfinic acid is added to solutions of ferric salts that are so dilute as to yield a scarcely perceptible pink coloration with thiocyanates.

A number of tetravalent ions, such as cerium, thorium, and uranium, react with benzenesulfinic acid in acid solution to yield precipitates corresponding to the formula  $(\text{C}_6\text{H}_5\text{—SO}_2)_4\text{M}$ , in which M represents one atom of the metal. Tin, titanium and zirconium are precipitated quantitatively in this way, although the sulfates do not correspond in composition to the above formula, but consist essentially of the hydrated oxides of tin and titanium and the basic zirconium salt.<sup>3,4</sup>

It is interesting to note that cerium, which is normally trivalent, and uranium which is usually hexavalent, form stable tetravalent benzenesulfates, although generally the salts of these metals in the tetravalent state are easily oxidized or reduced. It is also interesting to observe that although the sulfinic acids are easily oxidized to the corresponding sulfonic acids, and that ceric salts are powerful oxidizing agents, the compound  $(\text{C}_6\text{H}_5\text{—SO}_2)_4\text{Ce}$  is nevertheless formed in the reaction between these substances. Since abnormal valences are ordinarily stable only in complex salts, this fact strongly suggests that the sulfates of the tetravalent metals are not simple salts.

A study of the action of benzenesulfinic acid,  $\text{C}_6\text{H}_5\text{—SO}_2\text{H}$ , benzylsulfinic acid,  $\text{C}_6\text{H}_5\text{—CH}_2\text{—SO}_2\text{H}$ , and cyclohexylsulfinic acid,  $\text{C}_6\text{H}_{11}\text{—SO}_2\text{H}$ , reveals that only benzenesulfinic acid forms slightly soluble salts with the above-mentioned metal ions. This further indicates that the selective precipitating action of the sulfinic acids is dependent upon the direct union of the sulfinic acid group to the aromatic ring, and that the aromatic group, because of its system of conjugated double bonds, is coordinated to the metal atom.<sup>3,4</sup>

Other sulfinic acids, such as  $\alpha$ -naphthalenesulfinic acid and  $\beta$ -naphthalenesulfinic acid, react like benzenesulfinic acid with ferric iron and the tetravalent ions in acid solution, and consequently these compounds exhibit a pronounced selectivity in their precipitating action.

Krishna and Singh<sup>2</sup> have used various sulfinic acids for the determination and separation of ferric iron. With the aid of these reagents iron can be separated from aluminum, chromium, nickel and cobalt. Since no precipitate is formed with ferrous salts, the use of the sulfinic acids makes possible the separation of the two forms of iron.



1. J. Thomas, *J. Chem. Soc.* **95**, 342 (1909).
2. S. Krishna and H. Singh, *J. Am. Chem. Soc.* **50**, 792-8 (1928) ; *C.A.* **22**, 1325 (1928).
3. F. Feigl, *Ind. Eng. Chem., Anal. Ed.* **8**, 406 (1936).
4. F. Feigl and V. Anger, *Specific and Special Reactions*, p. 119, Elsevier, New York (1940).

## BENZENESULFINIC ACID

$C_6H_6O_2S$

Mol. Wt. 142.17

Beil. Ref. XI, 2

$C_6H_5SO_2H$

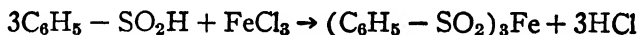
**Use:** Detection of cerium, iron, thorium, tin, titanium, uranium, and zirconium.

Determination of cerium, iron, thorium, tin, titanium, uranium, and zirconium.

Benzenesulfinic acid is obtained as prisms from water. It melts at 83-4° C. and decomposes above 100° C. It is readily soluble in hot water, alcohol, and ether, but is only slightly soluble in cold water.

**Preparation:** Mix 20 g. of benzenesulfonyl chloride with 50 g. of sodium sulfite,  $Na_2SO_3 \cdot 9H_2O$ , and 100 g. of crushed ice, and then shake the mixture for 3 hours until solution is complete. Test for alkalinity from time to time, and add dilute sodium hydroxide to prevent the formation of sulfur dioxide. Keep cold by frequent additions of ice, since the temperature must not be permitted to rise. Filter and acidify slowly with cold concentrated hydrochloric acid. The sulfinic acid separates at this point as a crystalline mass. Recrystallize and dry thoroughly in a vacuum desiccator.

**Determination of iron.** Iron may be determined by a gravimetric method based upon the precipitation of iron by the addition of benzenesulfinic acid to an acid solution of the ferric salt. This precipitate is ignited to ferric oxide. Krishna and Singh<sup>1</sup> have also used a titrimetric method for iron in which an acid ferric chloride solution is titrated with a standard solution of benzenesulfinic acid, using potassium thiocyanate as an external indicator. The iron present is calculated from the equation



The reagent is prepared as follows:

**Reagent.** Add 10 g. of benzenesulfinic acid to 1 liter of boiling water. If the acid is added to cold water, and the mixture then heated, the sulfinic acid usually changes to the insoluble disulfoxide and disulfone.

The method is said to be quite accurate.

1. S. Krishna and H. Singh, *J. Am. Chem. Soc.* **50**, 792-8 (1928) ; *C.A.* **22**, 1325 (1928).

**$\alpha$ -NAPHTHALENESULFINIC ACID** $C_{10}H_8O_2S$ 

Mol. Wt. 192.22

Beil. Ref. XI, 15

 $C_{10}H_7-SO_2H$ 

**Use:** Determination of cerium, iron, thorium, tin and uranium.

$\alpha$ -Naphthalenesulfinic acid is a crystalline solid melting at 84-85° C. It is only slightly soluble in ether and water containing hydrochloric acid. It is more soluble in pure water, and is moderately soluble in alcohol.

**Preparation:** Use the method described for benzenesulfinic acid, but substitute  $\alpha$ -naphthalenesulfonyl chloride for benzenesulfonyl chloride.<sup>1</sup>

**Determination of iron and the tetravalent metals.**  $\alpha$ -Naphthalenesulfinic acid is used in exactly the same manner as benzenesulfinic acid for the determination of ferric iron, cerium, thorium, tin and uranium. Krishna and Singh<sup>1</sup> especially recommend  $\alpha$ -naphthalenesulfinic acid and its  $\beta$ -isomer for this purpose. Dubsky and co-workers<sup>2</sup> report, however, that the ferric salts are filtered, ignited, and titrated only with considerable difficulty, and that these reagents are not as satisfactory as others which have been proposed for the iron determination.

1. S. Krishna and H. Singh, *J. Am. Chem. Soc.* **50**, 792-8 (1928); *C.A.* **22**, 1325 (1928).

2. J. V. Dubsky, E. Oravec, and A. Langer, *Chem. Obzor.* **12**, 41-5 (1937); *C.A.* **31**, 5712 (1937).

 **$\beta$ -NAPHTHALENESULFINIC ACID** $C_{10}H_8O_2S$ 

Mol. Wt. 192.22

Beil. Ref. XI, 16

 $C_{10}H_7-SO_2H$ 

**Use:** Determination of cerium, iron, thorium, tin, and uranium.

$\beta$ -Naphthalenesulfinic acid is a crystalline solid melting at 105° C. It is soluble in water, alcohol, and ether.

**Preparation:** Use the method described for benzenesulfinic acid, but substitute  $\beta$ -naphthalenesulfonyl chloride for benzenesulfonyl chloride.<sup>1</sup>

**Determination of iron and the tetravalent metals.** This compound is used in the same manner as its  $\alpha$ -isomer (see above) for the determination of iron and the tetravalent metals.

1. S. Krishna and H. Singh, *J. Am. Chem. Soc.* **50**, 792-8 (1928); *C.A.* **22**, 1325 (1928).

2. J. V. Dubsky, E. Oravec, and A. Langer, *Chem. Obzor.* **12**, 41-5 (1937); *C.A.* **31**, 5712 (1937).

## CHAPTER VIII

### SELENINIC ACIDS

The seleninic acids can be used in analysis in a manner similar to the sulfinic acids. The seleninic acids form insoluble yellow salts with ferric iron, and in strongly acid solutions also precipitate stannic, ceric, thorium, and uranium salts. A direct combination of the seleninic acid group with an aromatic nucleus is necessary for precipitation. It appears probable that these compounds can be used for the microdetermination and separation of the above mentioned metals.<sup>1</sup>

The seleninic acids behave differently from the sulfinic acids in that they react in acid solutions with molybdates and tungstates to form white precipitates. Further, all seleninic acids in which the  $\text{SeO}_2\text{H}$  group is attached to either an aromatic or aliphatic radical give this reaction. The precipitates formed, however, are not simple salts, but are complex molecular compounds, possibly of the heteropoly acid type.<sup>1,2</sup>

1. F. Feigl, *Ind. Eng. Chem., Anal. Ed.* **8**, 406 (1936).
2. F. Feigl, *Specific and Special Reactions*, p. 120, Elsevier, New York (1940).

## CHAPTER IX

### THE ALKALOIDS

The term alkaloid is generally applied to basic nitrogenous compounds of natural origin. Many of these substances have been used in analytical procedures. These uses are usually based on their basic, salt-forming character or upon their reducing properties. These reagents have proved especially useful for the detection and determination of bismuth, antimony, tin, gold, arsenic, phosphorus and the platinum metals.

#### APOMORPHINE

$C_{17}H_{17}O_2N$

Mol. Wt. 267.14      Beil. Ref. XXI, 187 (246)

**Use:** The detection of antimony pentachloride, arsenate, chlorine, nitrite, oxidizing agents and titanium.

This alkaloid occurs as colorless crystals, which rapidly become green in air due to oxidation. It is slightly soluble in water, sparingly soluble in benzene and ether, but is soluble in alcohol, acetone and chloroform.

**Detection of nitrite.** Pavelka <sup>1</sup> has used apomorphine for the detection of nitrites.

**Procedure.** Add 2-3 drops of 50 per cent acetic acid to a dilute solution of the material to be tested, and then add 1-2 mg. of apomorphine. Heat nearly to boiling, cool, and shake with ethyl acetate. A violet color appears if nitrite is present. This reaction is obtained with solutions having a dilution of 1:15 million.

This test may also be used for the detection of a nitrate after reducing to the nitrite. Nitrites, of course, must be absent or previously removed.

**Detection of chlorine and oxidizing agents.** Pesetz <sup>2</sup> has used apomorphine for detecting chlorine and other oxidizing agents.

**Procedure.** Mix an alcoholic solution of apomorphine with three times its volume of concentrated sulfuric acid and heat on a water-bath. Cool and carefully dilute with water. An intense orange-red color appears if oxidizing agents, such as hypochlorous acid, bromine-water or nitrites are present.

**Reaction with antimony pentachloride and arsenate.** Apomorphine hydrochloride reacts with antimony pentachloride in a chloroform solution to give a ruby-red color. A sulfuric acid solution of apomorphine is colored dark blue by the addition of sodium arsenate, followed by gentle warming.<sup>3</sup>

**Detection of titanium.** Apomorphine in concentrated sulfuric acid reacts with titanium to give a light red-brown color.<sup>4,5</sup>

1. F. Pavelka, *Mikrochemie*, **8**, 46-52 (1930); *C.A.* **24**, 1600 (1930).
2. M. Pesez, *Bull. soc. chim.* [5] **3**, 675 (1936).
3. L. Ekkert, *Pharm. Zentralhalle*, **75**, 49, 50 (1934).
4. R. D. Hall and E. F. Smith, *J. Am. Chem. Soc.* **35**, 138-45 (1913).
5. R. D. Hall and E. F. Smith, *Proc. Am. Phil. Soc.* **44**, 196 (1905).

## ASPIDOSPERMINE

$C_{22}H_{30}O_2N_2$

Mol. Wt. 354.25

**Use:** Detection of selenium in sulfuric acid.

Aspidospermene occurs as white needles or prisms. It melts at 208° C. and boils at 220° C. at 2 mm. The compound is a weak base. It is insoluble in water, soluble in alcohol, benzene, ether, chloroform, and dilute acids.

**Detection of selenium.** Aspidospermene has been used by Palet<sup>1</sup> for the detection of selenium in sulfuric acid.

**Procedure.** Add a small crystal of the alkaloid to a drop or two of the sulfuric acid to be tested, and heat over the flame of a Bunsen burner until fumes of sulfur trioxide are given off. If selenium is present, a deep violet coloration appears, first at the surface of the crystal, and finally throughout the liquid.

Pure sulfuric acid does not give this reaction, and there is no interference from oxidizing agents, such as potassium chlorate or lead peroxide, which give red colorations.

1. L. P. J. Palet, *Ann. chim. anal.* **23**, 25-6 (1918); *C.A.* **12**, 1028 (1918).

## ATROPINE SULFATE

$(C_{17}H_{23}O_3N)_2 \cdot H_2SO_4$

Mol. Wt. 694.47

Beil. Ref. XXI, 27 (198)

**Use:** Detection of gold.

Atropine sulfate consists of white granules or powder. It is intensely poisonous. It melts at 190-194° C. It is soluble in water, alcohol and glycerol, but is only very slightly soluble in chloroform and is insoluble in ether.

**Detection of gold.** A dense mass of tiny liquid globules forms immediately when a drop of atropine sulfate solution is added to a dilute solution of gold chloride. Upon stirring the drop vigorously with a glass rod, many thin, bright yellow, rectangular plates appear. This reaction may be used for the microchemical detection of gold.<sup>1</sup>

1. W. F. Whitmore and H. Schneider, *Mikrochemie*, **17**, 279-319 (1935).

## BERBERINE

$C_{20}H_{19}O_5N$

Mol. Wt. 353.16

**Use:** Detection of nitrate.

Berberine is an alkaloid obtained from various plants. The base is unstable and is known only in aqueous solution. The hydrochloride is a yellow crystalline solid, which is slightly soluble in water and is insoluble in alcohol, chloroform and ether.

**Detection of nitrate.** When a drop of berberine hydrochloride solution and a drop of sulfuric acid are added to a drop of a solution containing a nitrate or nitric acid, a dark brownish-red color is obtained. Hydrochloric acid produces the same effect upon warming.<sup>1</sup>

1. C. Reichard, *Chem.-Ztg.* **30**, 790 (1906).

## BRUCINE

$C_{23}H_{26}O_4N_2$

Mol. Wt. 466.28

**Use:** Detection of antimony, arsenic, bismuth, cadmium, cerium, chlorate, chromium, columbium, copper, lead, mercury, nitrate, perchlorate, persulfate, rhenium, tin and zinc.

Determination of cadmium, cerium, nitrate, persulfate and vanadium.

Brucine is an alkaloid obtained from *Nux Vomica* and *Ignatia* seeds. It consists of white, bitter crystals, or is a crystalline powder. It is *very poisonous*. It melts when anhydrous at about 178° C., and becomes anhydrous at 100° C. It behaves as a monoacid base. It dissolves in 320 parts of water, or 150 parts of boiling water. It is soluble in alcohol, methanol, and chloroform, but it is only slightly soluble in benzene and ether.

**Detection of nitrate.** In 1863 Kersting<sup>1-3</sup> first observed that a solution of brucine in concentrated sulfuric acid turns red in the presence of nitric acid or nitrates. This reaction has been used with various modifications as a sensitive test for nitrates, or for the colorimetric determination of nitrates. The test was originally performed as follows: <sup>3</sup>

**Procedure.** Mix 1 ml. of a solution of one part of brucine in 1000 parts of water with 1 ml. of the solution to be tested, and pour concentrated sulfuric acid into the mixture carefully so as to form 2 layers. A red ring is formed if nitrate is present.

The test was performed by Pickard<sup>4</sup> by adding brucine to a mixture of equal volumes of hydrochloric acid and the solution to be tested. The sensitivity is 1:640,000.

The method of Kersting has been modified by Cazeneuve and Defournel<sup>5</sup> for the detection of nitrate in water.

**Procedure.** Evaporate one liter of water to be tested to dryness. Add 20 ml. of water and 50 mg. of brucine and again evaporate to dryness. To this residue add a few drops of formic acid and a little hydrogen peroxide. A pink color forms in 15 minutes if nitrate is present. The sensitivity is 0.1 mg. of nitrate per liter of water.

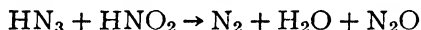
The brucine test may be carried out by a spot technique as follows:

**Reagent.** Dissolve 0.02 g. of brucine in 100 g. of concentrated sulfuric acid. Sulfuric acid usually contains sufficient nitrate or nitrite to give a rose color with brucine. The acid can be freed from this interference, however, by diluting to a specific gravity of 1.4, and then carefully heating to the boiling point.

**Procedure.** Mix a few drops of the reagent on a spot plate with a few drops of the solution to be tested. In the presence of a nitrate a red color appears, but this changes on standing to a yellowish-red. As little as 0.06% of nitric acid can be detected at a concentration of 1:800,000.

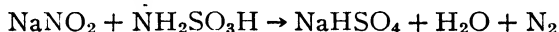
Chlorates and nitrites give a similar color reaction with brucine, and consequently must be removed before performing the nitrate test. Interference by nitrite may be eliminated by the use of sodium azide, aminosulfonic acid, and urea as follows:

(a) *Sodium azide.* The removal of nitrite with sodium azide is complete in an acid solution. The reaction takes place according to the following equation:



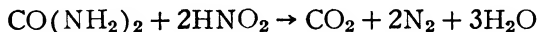
In order to test for nitrates in the presence of nitrites, add sodium azide to the acid solution to be tested, allow to stand for a short time, and then boil to complete the reaction and to expel the volatile hydrogen azide. Cool, and test the solution with brucine as described above.

(b) *Aminosulfonic acid:* Nitrites are destroyed by aminosulfonic acid according to the following reaction:<sup>6</sup>



In concentrated solutions the reaction is completed within about one minute, although in dilute solutions the reaction is almost instantaneous. A 0.5 per cent solution of aminosulfonic acid is used, and the reaction is both rapid and complete.

(c) *Urea:* Urea reacts with nitrous acid according to the following equation:



Nitrites may be removed by this method before testing for nitrate with brucine, but in the presence of urea the sensitiveness of the reaction is decreased from 0.2-0.3 mg.  $\text{N}_2\text{O}_5$  per liter to 0.5-0.6 mg. of  $\text{N}_2\text{O}_5$  per liter.<sup>8</sup>

The brucine reaction has been used by Agostini,<sup>7</sup> Korenman,<sup>9</sup> Hinrichs,<sup>10</sup> and Gutzeit<sup>11</sup> as a separate test for nitrate, and by Agostini<sup>12</sup> as a test for nitrate in a systematic scheme of analysis of the common anions.

Seiler<sup>49</sup> has used this reaction for the detection of nitrates in distilled water.

**Determination of nitrate.** Nitrates may be estimated colorimetrically by their reaction with brucine in the presence of sulfuric acid. Lunge L.woff<sup>13</sup>

originally recommended as the reagent a solution of 0.2 g. of brucine in 100 ml. of concentrated sulfuric acid. Hasse,<sup>14</sup> however, reports that a solution of brucine in chloroform is preferable for the nitrate determination. The sample should contain 0.01-0.2 mg. of nitrate nitrogen. The color is intense and stable for many hours. The determination is made by the sulfur-yellow color which follows the initial red color, since measurements of the latter are not reliable.

Nitrous acid interferes with the determination of nitric acid.<sup>18</sup> Winkler<sup>19-23</sup> has made a study of the reactions of brucine with nitric and nitrous acids, and reports the following results:

(a) The reaction of brucine with nitrous acid in the presence of sulfuric acid depends upon the proportion of sulfuric acid present. If equal volumes of concentrated sulfuric acid and water are used, a deep red coloration appears; with 2 volumes of acid and 1 volume of water, a rose color is obtained; but with 4 volumes of sulfuric acid and 1 volume of water, there is no reaction due to the formation of nitrosyl sulfuric acid.

(b) Nitrates give no reaction unless the acid is strong. With 2 volumes of water to 1 volume of sulfuric acid there is no coloration, but with 1 volume of water to 2 volumes of sulfuric acid, nitrates cause a coloration. In this way it is possible to detect nitrates and nitrites separately.

These findings have been confirmed by Lunge.<sup>24,25</sup>

Thus, if nitrite is not to be determined with nitrate, 2 parts of sulfuric acid must be present for 1 part of water. If nitrates and nitrites are to be determined together, decrease the amount of sulfuric acid so that the mixture will contain 2 parts of water for 1 part of sulfuric acid.

If the sample contains much organic matter or ferrous iron, oxidize by the careful addition of a slight excess of 0.1 per cent solution of potassium permanganate. Nitrite is oxidized to nitrate by this procedure, and if nitrate is to be determined in the presence of nitrite, the nitrite concentration must be determined separately and deducted from the total nitrate found by the brucine determination.

**Reagents.** *Brucine reagent:* Dissolve 5 g. of brucine in 100 g. of pure chloroform. This solution is pale yellow in color, and is stable for several weeks.

*Standard nitrate solution:* Dissolve 0.7216 g. of pure potassium nitrate in sufficient water to make 1 liter of solution. This solution contains 0.1 mg. of nitrate nitrogen per ml.

**Procedure.** Place 10 ml. of sample, containing 0.01-0.2 mg. of nitrate nitrogen, in a 50-ml. volumetric flask, and place 10 ml. of distilled water in a similar flask. To the flask containing the water, add a quantity of the standard nitrate solution until the concentration is approximately equal to that of the unknown. To both sample and standard add 0.2 ml. of the brucine reagent and 20 ml. of concentrated sulfuric acid. Allow to stand until the color changes to yellow. Cool quickly, and dilute each to 50 ml. with water or sulfuric acid,



depending on whether or not nitrite is to be determined. Compare the colors at any time within 24 hours.

Bycichin<sup>15</sup> has suggested the following modification of the brucine method for the determination of nitrate:

**Procedure.** Dissolve 0.2 g. of brucine in 10 ml. of chloroform, and add 1 ml. of this solution to 10 ml. of the solution to be analyzed, and then add 21 ml. of concentrated sulfuric acid. Cool and measure the color in a Hellig comparator.

This method is suitable for determining 0-18 mg. of  $N_2O_5$  per liter.

Autenrieth and Funk<sup>16</sup> have also used brucine for the colorimetric determination of nitrates, but Alten and Weiland<sup>17</sup> claim that this method gives variable results.

Eldson and Sutcliff<sup>26</sup> have used brucine for determining nitrates in milk; Tillmans and Splittgerber<sup>27</sup> have used a similar method for determining potassium nitrate in meat; and Sefton<sup>28</sup> has studied this procedure for determining nitric acid in battery acid.

**Detection of cadmium.** Solutions of cadmium salts in dilute sulfuric acid yield with brucine and potassium bromide a white crystalline precipitate of  $[(CH_3O)_2C_{21}H_{20}O_2N_2]_2 \cdot CdBr_2 \cdot 2HBr$ .<sup>50</sup> Meurice<sup>29</sup> has made this reaction the basis for a sensitive test for cadmium. This reaction is also of interest since it affords a satisfactory method for distinguishing between bromides and chlorides. Chlorides, except mercuric chloride, do not give this reaction.

Cadmium may be detected as follows:

**Procedure.** To the solution to be tested in a test tube, add 1 ml. of a 1 per cent solution of brucine and a little potassium bromide. A white precipitate of the double bromide forms if cadmium is present.

Copper does not interfere under the conditions of the test. After detecting copper by means of the blue color of the ammonia complex in the usual scheme of analysis, cadmium can be detected by means of the brucine test after acidifying a portion of the solution with sulfuric acid.

Martini<sup>30,31,50</sup> and Korenman<sup>32,33</sup> have used the brucine reaction as a sensitive microchemical test for cadmium salts. The double bromide of cadmium and brucine crystallizes in monoclinic prisms grouped in rosettes. The test is carried out as follows:<sup>31</sup>

**Procedure.** To a small drop of a 1 per cent solution of cadmium chloride on a cover glass, add an equal quantity of concentrated sodium bromide solution, and then allow a small quantity of concentrated brucine acetate to run to the edges of the mixture. A white precipitate forms at once. Salts of other metals do not interfere.

According to Korenman,<sup>34</sup> as little as 0.12γ of cadmium can be detected in solutions of other metal ions, and 0.6-1.2γ in solutions containing the ions

shown in Table 36. The limiting relative concentrations of cation per unit of cadmium are also shown.

TABLE 36.—INTERFERENCE OF METALS WITH THE CADMIUM TEST

Cation	Limiting Conc.	Cation	Limiting Conc.
Zinc	170	Calcium	300
Cobalt	170	Manganese	400
Nickel	1000	Bismuth	600
Lead	1000	Tin	440
Copper	550	Antimony	120
Silver	280	Mercury	370
Chromium	120	Magnesium	160
Aluminum	70	Strontium	700
Iron	300	Barium	430

**Determination of cadmium.** Nikitina<sup>35</sup> has used the brucine reaction of Meurice for the determination of cadmium in aluminum-magnesium alloys. Cadmium may be precipitated from dilute sulfuric acid solution with brucine and potassium bromide, while magnesium, copper, zinc, manganese, and aluminum remain in solution. The method for the determination is as follows:

**Procedure.** Dissolve 0.3 g. of the sample to be analyzed in 10-15 ml. of 20 per cent sulfuric acid, evaporate to 5 ml., and filter off any silica. Add in quick succession, 5 ml. of 1 per cent brucine in 20 per cent sulfuric acid (for a minimum of 5 mg. of cadmium), and 10 ml. of 10 per cent potassium bromide. Stir vigorously until precipitation is complete, and allow to stand for one hour, and finally filter with suction through a tared glass filter crucible. Wash the precipitate 5-6 times with a solution prepared by mixing 40 ml. of 1 per cent brucine sulfate, 30 ml. of 10 per cent potassium bromide, and 80 ml. of water, and then 8 times with a mixture of one part of ethyl alcohol and 7 parts of ether. Dry at 130-50° C. for 30 minutes and weigh. The cadmium factor is 0.092.

To determine cadmium in aluminum alloys, dissolve 0.5 g. of the sample in a little hydrochloric acid, evaporate with 3 g. of sulfuric acid to fumes, dissolve the residue in water, filter from silica, evaporate to 10-20 ml., and proceed as above.

Thompson<sup>36</sup> has proposed the use of brucine for the determination of cadmium in the presence of zinc. The separation of cadmium from zinc by means of hydrogen sulfide is tedious and time consuming, and may be eliminated by precipitating cadmium with a mixture of brucine sulfate and potassium iodide.

**Procedure.** To the lead-free solution containing 20-30 mg. of cadmium, add 1.5 ml. of 1 per cent brucine sulfate and 1.5 ml. of potassium iodide solution for each mg. of cadmium present (approximately). Allow to stand for 10 minutes, filter, wash first with a mixture of equal parts of brucine and potassium iodide reagent, and finally with a mixture of 1 part of ethyl alcohol and 4 parts of toluene. Dissolve the precipitate in 100 ml. of hot water, add 5 ml. of 0.5

per cent eosin Y as indicator, and titrate the iodide with 0.03 N silver nitrate to the adsorption end-point. Compare the titration value with that obtained using solutions containing a known quantity of cadmium.

Results obtained using this method are shown in Table 37, which is taken from the work of Thompson.<sup>36</sup>

TABLE 37.—SEPARATION OF ZINC AND CADMIUM

Cd Present g.	Cd Found g.	Zn Present g.	Pb Present g.	Ratio of Zn to Cd	Error mg.
0.0200	0.0201	40.005	0.500	1000:1	+0.1
0.0201	0.0201	0.020	....	1:1	0.0
0.0250	0.0249	0.100	....	4:1	-0.1
0.0302	0.0302	0.270	....	9:1	0.0
0.0301	0.0302	0.003	0.300	1:10	+0.1
0.0400	0.0402	2.000	....	50:1	+0.2
0.0502	0.0503	0.100	0.075	2:1	+0.1
0.0500	0.0500	0.0025	0.022	1:20	0.0

**Detection of copper and lead.** Solutions of copper and lead salts react with brucine and potassium iodide to form precipitates which may be used for the detection of these ions.<sup>33</sup>

**Procedure.** To 1 ml. of a solution of a salt of copper or lead, add 1-3 drops of a saturated solution of potassium iodide and a little brucine. With lead, a yellow or white turbidity forms at dilutions as low as 1:500,000, and with copper a yellow precipitate appears. The sensitivity of the copper reaction is 1:300,000.

**Detection of bismuth.** Reichard<sup>37</sup> claims that very small quantities of bismuth can be detected by means of a red coloration obtained with an excess of brucine. Moser,<sup>38</sup> however, has been unable to duplicate these results.

Korenman<sup>33</sup> recommends brucine and potassium iodide for the detection of bismuth in very dilute solutions.

**Procedure.** To 1 ml. of the solution to be tested, add 1-3 drops of a saturated solution of potassium iodide, and a few drops of a solution of brucine. A yellow precipitate, insoluble in hydrochloric acid, forms if bismuth is present. The sensitivity of this reaction is 1:720,000.

Korenman<sup>32</sup> has also used brucine and potassium bromide for the micro-detection of bismuth. As little as 0.4 $\gamma$  of bismuth can be detected by this method. Dubsky and Trtilek<sup>39</sup> have studied the use of brucine as a reagent for bismuth.

With sodium or potassium iodide and brucine, 5 $\gamma$  of bismuth can be detected in 5 ml. of solution.<sup>33</sup>

When brucine citrate is added to a solution containing bismuth and an alkali iodide, a yellowish-orange precipitate is formed, and this changes after about 1 minute to an intense brick-red precipitate.<sup>59</sup> This reaction may be applied in

any acid solution. When used as a spot test it is capable of detecting 0.3 $\gamma$  of bismuth at a limiting concentration of 1:100,000.

**Reagents.** *Brucine citrate*: Dissolve 100 g. of citric acid in 100 ml. of water, add 12 g. of brucine, and heat until solution is complete.

*Borate inhibitor*: Mix equal volumes of 1 M boric acid and 1 M sodium borate.

**Procedure.** On a spot plate, place 1 drop of the solution to be tested, and to it add 1 drop each of the borate inhibitor, saturated aqueous sodium bisulfite, brucine citrate, and 20 per cent aqueous potassium iodide. A brick-red precipitate forms if bismuth is present.

There is no positive interference with this test. Cadmium, copper, lead, mercury, and silver interfere by preventing the full development of the red color, and thereby reducing the sensitivity of the test. The bismuth color is masked by the colors formed in reactions with thallous, mercurous, palladous, and tellurite ions. In this way 3.1 $\gamma$  of bismuth can be detected in 5 ml. of solution.

**Detection of mercury.** Korenman<sup>32</sup> suggests the following microchemical method for detecting as little as 0.5 $\gamma$  of mercury:

**Procedure.** To a drop of the solution to be tested, on an object glass, add 1 drop of a cold solution of brucine in dilute sulfuric acid, and then 1 drop of 5 per cent potassium or sodium bromide. With mercury characteristic crystals form, or, at low concentrations, an amorphous precipitate appears.

The test may also be carried out in a test tube. A saturated solution of brucine in 5 per cent acetic acid is used as the reagent. Potassium iodide is added in a saturated solution.<sup>33</sup>

**Detection of antimony, arsenic, and zinc.** Solutions of antimony salts in dilute hydrochloric acid form characteristic crystals when treated with brucine and potassium bromide as described for the mercury test.<sup>32</sup> Only 0.3 $\gamma$  of antimony can be detected in this manner.

A concentrated solution of arsenic acid gradually forms a greenish-yellow precipitate. Zinc also gives a crystalline precipitate. A yellow precipitate is obtained with antimony at concentrations as low as 1:1,300,000 when potassium iodide is substituted for potassium bromide.<sup>33</sup>

Wagenaar<sup>60</sup> reports that 2 $\gamma$  of zinc can be detected by the microscopic examination of the crystals which are formed with brucine.

**Detection of tin.** Deniges<sup>40</sup> has used brucine to detect stannous tin by means of the following reaction:

**Procedure.** Dissolve 0.1 g. of brucine in a mixture of 1 ml. of cold nitric acid and 50 ml. of water, and heat to boiling for 15 minutes. This yellow solution is colored reddish-violet by stannous salts.

Tin gives an amorphous precipitate when treated with brucine and potassium bromide.<sup>32</sup>

**Detection of cerium.** Ceric salts react with brucine in acetic acid to form a stable pink color or an orange-red color at higher concentrations. The pink color is visible at a concentration of only 0.001 mg. of cerium per ml. Lanthanum, thorium, and trivalent cerium do not give color reactions with brucine. In an alkaline medium, brucine yields a dark brown precipitate with tetravalent thorium, and a colorless, gelatinous precipitate with trivalent cerium, thorium, and lanthanum. The reaction of tetravalent cerium and brucine is attributed to the oxidizing action of ceric ions.<sup>41,61</sup>

Cerium is best detected by means of a test tube reaction, since the pink color can scarcely be detected in thin layers. The reaction is more sensitive when carried out on a filter paper than as a drop reaction. The test is made by acidifying slightly the solution to be tested with sulfuric acid, and then adding a solution of the reagent in acetic acid.<sup>42</sup>

**Determination of cerium.** The color formed in the reaction between cerium and brucine follows the Lambert-Beer law, and consequently can be used for the colorimetric determination of cerium. The intensity of the coloration of the solution depends on the length of time which elapses after its preparation. A red color is first formed, and this changes to orange and finally brown. Best results are obtained when the solution is allowed to stand 15-20 hours,<sup>43</sup> although the color intensity is practically constant after 5-10 minutes.

**Procedure.** The sample solution should have a volume of about 10 ml., and should contain only a few tenths of a milligram of cerium. Make approximately 1 N in sulfuric acid, and add 0.2 g. ammonium persulfate and 0.5 mg. of silver nitrate. Boil gently 10 minutes, adding water if necessary, to ensure the decomposition of all persulfate. Cool the solution to room temperature, add 0.25 ml. of 0.1 per cent brucine in 1 N sulfuric acid. Dilute to a suitable volume, and determine the transmittancy of the solution after 10 minutes, using a blue filter. A second reading should be made after 10 minutes to make certain that the transmittancy does not change due to the presence of unchanged persulfate. The color may also be compared with suitable standards.

Permanganate produces a yellow color. Chromate oxidizes brucine slowly in an acid solution to form a brown color. Ferric iron does not interfere in small amounts. Persulfate slowly forms a yellow-brown color.

**Determination of vanadium.** Jilek and Vicovsky<sup>44</sup> have used brucine for the quantitative precipitation of vanadium. When 100 ml. of a dilute solution of sodium vanadate (containing 7-124 mg. of  $V_2O_5$ ) is treated with a slight excess of brucine in 20 per cent acetic acid, a precipitate is obtained which can be ignited to  $V_2O_5$ . Results obtained using this procedure agree with those (such as mercurous nitrate method of Rose) employing more tedious methods. The determination cannot be carried out in the presence of chromates, but interference due to this ion can be eliminated with the use of quinoline.

**Detection of chromium.** Brucine yields crystalline compounds with chromates and dichromates, which may be used for the microchemical detection of the latter. In this way 5γ of chromate can be detected at a dilution of 1:2000. The reaction with dichromate is somewhat more sensitive. Mercuric, cadmium,

zinc, ferrocyanide, ferricyanide, iodide and thiocyanate ions and free iodine and bromine interfere.<sup>60,62</sup>

**Detection of rhenium.** Rhenium trichloride dissolves in hydrochloric acid to form  $\text{HReCl}_4$ , which reacts with brucine to form a crystalline compound that can be used for the microscopic detection of rhenium.  $\text{H}_2\text{ReCl}_6$  also forms a crystalline compound with brucine.<sup>45,52-54,61</sup> This reaction is not very sensitive.<sup>55</sup>

**Detection of columbium.** Various alkaloids, including brucine, have been used in color reactions for columbium,<sup>63-66</sup> but these tests are not recommended.

**Detection and determination of persulfates.** Ammonium persulfate reacts with brucine to give a coloration which is similar to that obtained with cerium.<sup>48</sup> Cerium may, however, be determined colorimetrically by means of brucine if the ammonium persulfate is decomposed before proceeding with the determination.

The reaction between ammonium persulfate and brucine may be used for the colorimetric determination of ammonium persulfate. When a solution of brucine acetate is added to a cold, pure solution of ammonium persulfate, the color is observed only after a few minutes, and from this point the color intensity increases on standing. The orange-red coloration is observed immediately when the solution is acidified with sulfuric acid.

Ammonium persulfate in an ammoniacal solution gives a yellow coloration with brucine, while cerium in an ammoniacal medium yields a color reaction only when the solution of brucine has been added to an acid solution of cerium to which, after the color has developed, ammonia is added.

**Detection of chlorates in the presence of hypochlorites.** A yellow color appears when 5 ml. of a 0.5 per cent solution of sodium hypochlorite is treated with 0.05 g. of brucine hydrochloride or sulfate, and 5 drops of dilute hydrochloric acid. This color turns to a cherry-red upon boiling, and this color remains unchanged when the solution is boiled with an additional 10 ml. of dilute acid. A solution of potassium chlorate similarly treated is not colored in the cold, and when boiled the solution at first becomes yellow, and then cherry-red, and this color is discharged if the solution is boiled with an additional 10 ml. of dilute hydrochloric acid. This decolorization on boiling with dilute hydrochloric acid is characteristic for chlorates.<sup>46</sup>

**Detection of perchlorates.** Deniges<sup>47,48</sup> reports that perchlorates form characteristic crystals when treated with a solution of brucine in acetic acid.

**Detection of titanium.** Brucine in concentrated sulfuric acid reacts with titanium to form a light red color.<sup>57,58</sup>

**Detection of the platinum metals.** Whitmore and Schneider<sup>56</sup> have studied the use of brucine as a microchemical reagent for the detection of the platinum metals. Their results are shown in Table 38, which is taken directly from their published work.

TABLE 38.—REACTIONS OF BRUCINE WITH THE PLATINUM METALS

Test Material	Description
RuCl <sub>3</sub>	Many, small, needle-shaped, crystals form immediately throughout the drop. These occur singly, also in radiating clusters. Some of the needles develop delicate branches
RhCl <sub>3</sub>	A yellowish-brown, amorphous precipitate forms immediately. On standing a short time many, small branching, moss-like forms appear throughout this precipitate
PdCl <sub>2</sub>	A very dense, yellow, amorphous precipitate forms immediately. There then develops throughout this precipitate a great many radiating clusters of crystals. These also occur singly as well defined, bright yellow hexagonal plates and trapezoids
Na <sub>2</sub> OsCl <sub>6</sub>	A dense, yellow precipitate forms immediately. This precipitate is composed of a mass of long, slender, needle-shaped crystals. They occur singly and in clusters, some have serrated edges
IrCl <sub>3</sub>	A dense, brown precipitate forms immediately. This precipitate is composed of a mass of irregular crystalline forms. At the edge these appear as X's, also as clusters
H <sub>2</sub> PtCl <sub>6</sub>	A dense, yellow precipitate forms immediately. This precipitate is composed of a mass of small, very irregular slender crystals. They occur singly and in crosses
AuCl <sub>3</sub>	A very dense, brown, amorphous precipitate forms immediately

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## CACOTHELINE

**Use:** Detection of cerium, columbium, europium, mercury, molybdenum, rhenium, rhodium, tin, titanium, tungsten, and vanadium.

**Determination of tin.**



Cacotheline is reported by Moufang and Tafel<sup>1</sup> to be the nitrate of the bisdimethylmononitrobrucine hydrate, and to have the formula,  $C_{20}H_{20}(OH)_2 \cdot (NO_2)_2N_2O_3 \cdot HNO_3$ . This compound is a yellow crystalline solid, which is only slightly soluble in water.

**Preparation:** Dissolve 20 g. of brucine in 400 ml. of 10 per cent nitric acid and heat the clear solution to 60-70° C. A red color appears after a few minutes, and cacotheline precipitates as a yellow solid. Allow to stand for four hours and filter. Wash the precipitate free from acid with a little cold water and alcohol, and then dry in a desiccator over sulfuric acid.<sup>2,3</sup>

An alternative method has been described as follows:

**Preparation:** Dissolve 39.4 g. of dry brucine in 200 ml. of 5 N nitric acid in the cold, and then warm to 50-60° C. for 15 minutes. The solution turns red, then reddish-yellow, and finally yellow crystals of cacotheline separate from the mixture. Allow to stand in the water for a few hours and filter off the crystals with suction. Wash the precipitate with 1 N nitric acid, acetone, and ether.

**Detection of tin.** When an aqueous solution of cacotheline is added to an acid solution containing stannous ions, a violet color appears. This is due to the formation of a reduction product of cacotheline of unknown composition.<sup>4-9, 20-22</sup> Certain other reducing substances, such as sulfites, thiosulfates and antimonous ions react in a similar manner. Ferrous salts, however, in the absence of fluorides and phosphates, do not give a color reaction with cacotheline, and so a solution of a tin salt which has been formed by reduction with metallic iron can be used for the tin test.

A test tube reaction, based upon the use of cacotheline, is less sensitive than the spot test which is described below:

**Procedure.** Impregnate a strip of filter paper with a saturated aqueous solution of cacotheline, and before the paper is entirely dry, add a drop of solution to be tested. A red circle or a red ring is formed on the yellow paper, depending upon the amount of tin present, and this in turn is surrounded by a colorless zone. In this way 0.2γ of tin can be detected. The dilution limit is 1:250,000.

A test tube reaction carried out by adding a few drops of cacotheline reagent to an acid solution of stannous salt will detect only 30γ of tin in 3 ml. of solution.

Antimonous ions alone, of all common cations, give a color reaction under the conditions of the test, and this only in concentrations greater than or equal to 0.01 molar. Reducing ions such as bisulfite, hydrosulfite, sulfite, thiosulfate and titanous salts interfere, as do such oxidizing agents as nitric acid, chromates and chromic and mercuric salts. Colored ions, such as cobalt, copper, iron, nickel, and some vanadates interfere. Molybdates also prevent the tin test by reacting with stannous salts.<sup>8</sup>

Tests have shown that columbium, uranium, molybdenum, tungsten, vanadium, chromium and titanium, after reduction with metallic lead in hydrochloric acid, react with cacotheline to give highly colored products, and these may interfere with the detection of tin.<sup>10</sup>

Nechamkin and Sanders<sup>23,27</sup> have used cacotheline for the detection of tin in metal coatings, and Flood and Smedsaas<sup>24</sup> have used the same reagent for the detection of stannic tin in chromatographic analysis. Rossi and Serantes<sup>26</sup> used cacotheline for the detection of tin in alloys of tin, lead and bismuth.

**Determination of tin.** The violet color formed in the reaction between stannous salts and cacotheline may be used for the colorimetric estimation of small amounts of tin.<sup>3</sup> In aqueous solution, a color is obtained with as little as 2 p.p.m. of stannous tin; in the presence of 30 milliequivalents of hydrochloric acid, the sensitivity is twice as great. Nitric acid prevents the reaction, and sulfuric acid lowers the sensitivity. The color develops in about 15 minutes in a hydrochloric acid solution, and in 45 minutes in water. The color fades in a few hours. According to Strafford<sup>28</sup> the color fades rapidly, and for this reason is not suitable for a colorimetric comparison. The following procedure, however, has been suggested:

**Procedure.** Add 0.1 ml. of a 0.25 per cent aqueous solution of cacotheline to 10 ml. of the tin solution. Mix and let stand until the maximum color develops. Compare the resulting color with that of a suitable standard having the same acidity as the sample, and prepared similarly and simultaneously. The reaction is more sensitive, and the color develops more rapidly if 1 ml. of concentrated hydrochloric acid is added to both standard and sample before adding the cacotheline reagent.

Interference with this determination is the same as that described above in the section on the detection of tin.

**Reactions with reducing substances.** Mention has been made of the fact that reducing ions, such as titanous, vanadyl and trivalent rhodium compounds, and the lower oxides of molybdenum, tungsten, and also columbium chloride reduce cacotheline to form colored products,<sup>10-12</sup> and consequently these ions may be detected in a manner similar to that employed for stannous ions. About 1γ of any of the above elements is sufficient to give a color reaction. The test may also be obtained when the acids of arsenic, antimony and tellurium are treated with zinc and hydrochloric acid, and then the reagent, but selenious acid does not respond to this test. Hydrogen selenide, cuprous chloride and mercurous chloride in the presence of hydrochloric acid also give color reactions with cacotheline, and the same is true of finely divided mercury, of ferrous sulfate in the presence of phosphoric acid or a soluble fluoride, and of the cobalt cyanide complex,  $\text{Co}(\text{CN})_6^{4-}$ . Numerous organic compounds also give this test.<sup>12</sup>

**Detection of vanadium.** Trivalent vanadium compounds, like stannous salts, react with cacotheline to form a violet colored compound. Using this reaction, vanadates can be detected after reduction by means of metallic zinc and hydrochloric acid.<sup>13,14</sup>

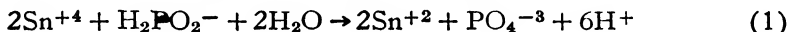
**Procedure.** On a spot plate mix a drop of the solution to be tested with a small piece of granulated zinc and a drop of hydrochloric acid, and then add a

drop of a saturated solution of cacotheline. A violet to red color appears if vanadium is present. As little as 1.2% of vanadium can be detected. The dilution limit is 1:25,000.

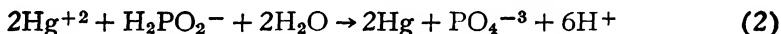
Molybdates and tungstates interfere with this test by reacting to form blue reduction products. Iron salts interfere only in the presence of phosphates or fluorides, since under these conditions ferrous ions also reduce cacotheline. Tin salts, of course, must be absent.

**Detection of rhenium.** A color reaction is obtained when rhenium compounds are reduced with zinc and hydrochloric acid and then treated with cacotheline,<sup>11</sup> but this reaction is not recommended by Wenger and Duckert<sup>25</sup> as a test for rhenium, since too many other substances give a similar reaction.

**Detection of mercury.** Mercury may be detected indirectly by an interesting application of the cacotheline test for stannous tin.<sup>15,16</sup> Stannic salts are reduced to stannous salts by hypophosphites according to the following equation:



This reaction, which normally proceeds very slowly, is remarkably accelerated by the addition of mercuric salts, which also react with hypophosphorous acid.



It appears that reaction (2) induces reaction (1), and that this induction takes place even in the presence of extremely small quantities of mercuric salts. Consequently mercury may be indicated indirectly by identifying stannous salts by means of the cacotheline reaction.

**Reagent.** The reagent used for the mercury test consists of a mixture of ammonium chlorostannate, sodium hypophosphite, and cacotheline, and is prepared as follows: Dissolve 10 g. of ammonium chlorostannate in 80 ml. 2 N of hydrochloric acid, allow to stand 24 hours, and filter. Mix this solution with 50 ml. of a 5 per cent sodium hypophosphite solution and 8 ml. of a 1 per cent cacotheline solution.

**Procedure.** Mix a drop of the above reagent with a drop of the solution to be tested in a micro-test tube, which is then suspended for 15 seconds over a boiling water-bath. According to the amount of mercury present, the yellow solution is colored light pink or red. For the most satisfactory results, run a blank when only very small amounts of mercury are present. As little as 0.1% of mercury can be detected by this method. The limit of dilution is 1:500,000.

The above test is successful even with solutions of undissociated mercuric cyanide or of the complex of sodium mercuric iodide. Gold, copper and palladium salts must be absent, since they also are reduced by hypophosphite, and their reduction products react with cacotheline in the same manner as stannous salts. Silver salts, and to an even greater extent, osmium salts reduce the catalytic action of mercury.<sup>17</sup>

**Detection of europium.** Bivalent europium, like titanium, tin, vanadium, columbium, molybdenum, tungsten, uranium, and rhenium, in the lower states of oxidation, reduces cacotheline to a violet dye. Other rare earth metals do not give a similar test, and consequently this reaction may be used for the detection of europium in a mixture of the rare earth metals. Europium is reduced prior to applying the cacotheline test by the use of zinc in the presence of hydrochloric acid.<sup>18</sup>

**Detection of cerium.** Cerous hydroxide reacts with cacotheline to give a color reaction, which may be used for the detection of cerium.<sup>19</sup>

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3. I. L. Newell, J. B. Ficklen, and L. S. Maxfield, *Ind. Eng. Chem., Anal. Ed.* **7**, 26-7 (1935); *C.A.* **29**, 1356 (1935).
4. J. Kisser and K. Lettmayr, *Mikrochemie*, **12**, 235-56 (1933); *C.A.* **27**, 678 (1933).
5. G. Gutzeit, *Helv. Chim. Acta*, **12**, 720 (1929).
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17. I. M. Kolthoff and R. S. Livingstone, *Ind. Eng. Chem., Anal. Ed.* **7**, 209 (1935).
18. G. Beck, *Mikrochim. Acta*, **3**, 141-3 (1938); *C.A.* **32**, 5333 (1938).
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## CAFFEINE

Synonym: Theine, guaranine, methyltheobromine, trimethylxanthine



Mol. Wt. 212.13    Beil. Ref. XXVI, 461 (136)

**Use:** Detection of antimony, bismuth, gold, osmium, and palladium.

**Determination of bismuth.**

Caffeine is usually obtained from tea, in which it occurs to the extent of about 1.5-3.5 per cent. It occurs as fleecy, white, odorless crystals, or as a white powder with a bitter taste. It usually occurs with 1 mole of water of hydration, which it loses upon exposure to air. It melts when anhydrous at 236-237° C. and sublimes at 178° C. It is soluble in water, alcohol, acetone, chloroform, ether and benzene. It is a weak base, and forms salts, but only with strong or moderately strong acids.

**Preparation:** Extract 100 g. of finely powdered tea with 400 ml. of alcohol, and add the alcoholic extract to a suspension of 50 g. of magnesium oxide in 300 ml. of water. Evaporate the mixture to dryness on a steam-bath in a porcelain dish with frequent stirring. Boil the residue once with 500 ml. of water, and then 3 times with 250 ml. of water. Filter while hot with suction. Add 50 ml. of dilute sulfuric acid to the combined filtrates, and concentrate by evaporation to about one third of their original volume. Filter, if necessary, while hot from the flocculent precipitate which occasionally forms, and extract 5 times with 30-ml. portions of chloroform. Decolorize the pale yellow solution by shaking, first with a few ml. of sodium hydroxide solution, and then with the same volume of water, and finally evaporate to dryness. Recrystallize the residue of crude caffeine from a little hot water.<sup>1</sup>

**Detection of bismuth.** Bismuth trichloride reacts with caffeine and potassium iodide to form an orange precipitate consisting of characteristic crystals. The precipitate disappears on heating and reappears when the mixture is cooled. Martini<sup>2,3</sup> has used this reaction for the microchemical detection of bismuth.

**Procedure.** Place a drop of the solution to be tested on a spot plate or a glass slide, and add one drop of 5 per cent solution of potassium iodide and 1 drop of an aqueous solution of caffeine. An orange precipitate forms if bismuth is present.

**Detection of antimony.** Caffeine may be used satisfactorily to replace quinoline and other nitrogenous compounds which have been used with potassium iodide in the Caille and Viel<sup>4</sup> reaction for antimony. A solution of antimony salt in 1:5 hydrochloric acid reacts with potassium iodide and an aqueous solution of caffeine to give a yellow precipitate. Martini<sup>2</sup> has used a similar method for the microdetection of antimony in minerals.

**Determination of bismuth.** Bismuth may be determined titrimetrically after precipitating with caffeine sulfate and potassium iodide by titrating with a standard potassium iodate solution. This method has been suggested by Beale and Chandlee.<sup>5</sup>

**Reagent.** Dissolve 133 g. of caffeine in 570 ml. of 6 N sulfuric acid and add sufficient water to make 1 liter of solution.

**Procedure.** Dissolve the sample containing about 30 mg. of bismuth in 10 ml. of concentrated sulfuric acid, and then remove most of the acid by evaporation. Dilute the resulting solution to 150 ml. in a 400-ml. beaker, and

add dropwise 30 ml. of the caffeine reagent and 25 ml. of 8 per cent potassium iodide solution. Allow to stand 10 minutes, filter, and wash 5 times with 15-ml. portions of a solution containing 1.5 g. of caffeine, 6 ml. of 6 N sulfuric acid, and 1 g. of potassium iodide per liter, and finally wash 4 times with 15-ml. portions of dibutyl ether. Digest the washed precipitate with 100 ml. of 5 per cent sodium hydroxide solution, and heat the mixture until decomposition is complete. Cool, add 23 ml. of concentrated hydrochloric acid, and 8 ml. of 0.5 M potassium cyanide solution, and finally titrate with a solution of potassium iodate containing 2.048 g. of potassium iodate per liter (1.0 ml. = 1 mg. of bismuth). Continue the addition of the iodate until the brown solution turns to a pale yellow, and then add 10 ml. of starch indicator solution, and titrate to the disappearance of the blue starch-iodine color.

This method gives accurate results for solutions containing 1.2-30 mg. of bismuth per liter. It is not satisfactory, however, in the presence of mercurous, silver or cupric ions, but mercuric salts do not interfere.

**Detection of palladium.** A drop of caffeine solution when added to a drop of solution containing a palladium salt causes the formation of a mass of irregular transparent leaf-like crystals.<sup>7</sup> This reaction has been used by Whitmore and Schneider<sup>6</sup> for the microdetection of palladium. This test can be used in the presence of all other metals of the platinum group. If gold is present, delicate bright yellow, needle-shaped crystals develop around the edge of the drop.

**Detection of gold.** Whitmore and Schneider<sup>6</sup> have also used caffeine for the microdetection of gold. When a drop of caffeine solution is added directly to a drop of solution to be tested, delicate, bright yellow, hair-like crystals arranged in tufts appear around the edge of the drop. Palladium does not interfere with this test. Gold is best detected by this reaction after it is extracted from its solution by means of ethyl acetate.

**Procedure.** To 0.5 ml. of the solution to be tested, add 1 ml. of ethyl acetate and shake vigorously. Allow to settle and draw off the ethyl acetate layer with the aid of a small pipet. Extract twice more with fresh portions of ethyl acetate. Combine the extracts and carefully evaporate to dryness, and then dissolve the residue in a little water and hydrochloric acid. To 1 drop of this solution add a drop of an aqueous solution of caffeine.

A summary of the reactions of caffeine with the metals of the platinum group, taken from the work of Whitmore and Schneider,<sup>6</sup> is shown in Table 39.

1. L. Gattermann and H. Wieland, *Laboratory Methods of Organic Chemistry*, Translated from 24th German ed., p. 405, Macmillan, London (1941).
2. A. Martini, *Pub. inst. investigaciones microquim., Univ. nacl. litoral*, **4**, 63-8 (1940); *C.A.* **36**, 1264 (1942).
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TABLE 39.—REACTIONS OF CAFFEINE WITH THE PLATINUM METALS

Test Material	Description
RuCl <sub>3</sub>	No apparent reaction
RhCl <sub>3</sub>	No apparent reaction
PdCl <sub>2</sub>	A very dense mass of irregular and transparent, leaf-like structures forms gradually. No definite crystalline forms can be recognized. (This test is good in the presence of the other elements of this group)
Na <sub>2</sub> OsCl <sub>6</sub>	On standing a short time some very bright, canary yellow plates appear around the edge of the drop. These have the form of parallelograms and occur singly and in clusters. A few, pale purple pyramids having six faces also appear around the circumference
IrCl <sub>3</sub>	No apparent reaction
H <sub>2</sub> PtCl <sub>6</sub>	No apparent reaction
AuCl <sub>3</sub>	On standing a short time sheaves of long, bright, yellow crystals form around the edge of the drop. Along the circumference there also appear at intervals dense masses of very fine, yellow hair-like crystals. As the drop evaporates, clusters of slender prisms appear throughout the drop. (This test is good in the presence of the other elements of this group.)

6. W. F. Whitmore and H. Schneider, *Mikrochemie*, 17, 279-319 (1935); *C.A.* 29, 6168 (1935).

7. H. J. Sandrus and M. L. Willard, *Mikrochemie* 12, 137 (1932); *C.A.* 27, 808 (1933).

## CINCHONAMINE

C<sub>19</sub>H<sub>24</sub>ON<sub>2</sub>

Mol. Wt. 296.20

**Use:** Detection and determination of nitrate.

The alkaloid cinchonamine is obtained from the bark of *Remijia Purdieana* Wedd., Rubiaceae. It is obtained as a white crystalline solid melting at 185° C. It is almost insoluble in water, but is soluble in alcohol, ether and dilute acids. The hydrochloride, which is commonly used as the analytical reagent, consists of white to yellowish crystals, which are very slightly soluble in water. The compound is freely soluble in alcohol.

**Detection and determination of nitrate.** Arnaud and Padé<sup>1</sup> first observed that the nitrate of cinchonamine is very insoluble, and suggested that perhaps the formation of this salt could be used for the detection and determination of nitrates. This reaction was later studied by Howard and Perry<sup>2</sup> and by Howard and Chick,<sup>3</sup> who recommend the use of cinchonamine as a precipitant in a gravimetric procedure for nitrates. They claim that satisfactory results may be obtained if the following points are carefully observed: (a) a large excess of reagent (0.6 g. of cinchonamine chloride for each 0.1 g. of potassium nitrate) must be used; (b) an excess of hydrochloric acid must be added on mixing the cinchonamine solution and solution to be analyzed; (c) the mixture must be allowed to stand for 12 hours before filtration; and (d) not more than 100 ml. of wash water for each g. of nitrate that is precipitated

should be used. The factor relating the weight of cinchonamine nitrate to potassium nitrate is 0.2813.

Although cinchonamine nitrate is one of the least water soluble of all the nitrates known, the formation of this compound is probably not as satisfactory a procedure for detecting nitrates as others which have been proposed. According to Howard and Chick,<sup>3</sup> a precipitate forms immediately when cinchonamine hydrochloride is added to a solution of potassium nitrate at a concentration of 1:1000. On standing a precipitate forms at a concentration of 1:100,000.

1. A. Arnaud, L. Padé, *Compt. rend.* **98**, 1488 (1884) ; **99**, 190 (1884).
2. B. F. Howard and F. Perry, *J. Soc. Chem. Ind.* **24**, 1281 (1905).
3. B. F. Howard and O. Chick, *J. Chem. Soc. Ind.* **28**, 53 (1909).

### CINCHONIDINE

Synonym: Cinchovatine,  $\alpha$ -quinidine

$C_{18}H_{22}ON_2$

Mol. Wt. 294.19    Beil. Ref. XXIII, 437(134).

**Use:** Detection of gold, iridium, osmium, palladium and platinum.

The alkaloid cinchonidine, a stereoisomer of cinchonine, is obtained from Cinchona bark. It occurs to the extent of 0.4 per cent in cultivated cinchona, and 2-3 per cent in native cinchona.

The compound consists of white, very bitter crystals, and melts at about 210° C. with decomposition. It is very slightly soluble in water, but is soluble in about 15 parts of alcohol, and 200 parts of ether. It is soluble in chloroform and dilute acids. The alkaloid and its salts are affected by light, and must be stored in a dark place or in a dark bottle.

Cinchonidine sulfate, which is commonly used as the analytical reagent, consists of white, silky, acicular crystals, which effloresce on exposure to air, and darken in light. The salt melts, when anhydrous, at about 240° C. with decomposition. One g. of the solid dissolves in 70 ml. of cold water, 20 ml. of hot water, 90 ml. of alcohol, 40 ml. of hot alcohol, and 620 ml. of chloroform. It is almost insoluble in ether. The aqueous solution is practically neutral.

**Reactions with the platinum metals.** Whitmore and Schneider<sup>1</sup> have used cinchonidine sulfate for the microdetection of the metals of the platinum group. Their results are summarized in Table 40, which is taken from their work:

1. W. F. Whitmore and H. Schneider, *Mikrochemie*. **17**, 279-319 (1935).

### CINCHONINE

$C_{19}H_{22}N_2O$

Mol. Wt. 294.19    Beil. Ref. XXIII, 420, 424.

**Use:** Detection of antimony, bismuth, cadmium, germanium and molybdenum.

Determination of bismuth, molybdenum, and tungsten.

Cinchonine is an alkaloid which occurs to the extent of 0.3-1.0 per cent in several species of Cinchona. It is a white to faintly yellow crystalline compound



which melts at about 260° C. It begins to sublime at 220° C. The alkaloid and its salts generally darken on exposure to light. It is almost insoluble in water and is only moderately soluble in alcohol, chloroform and ether.

TABLE 40.—REACTIONS OF CINCHONIDINE SULFATE WITH THE PLATINUM METALS

Test Material	Description
RuCl <sub>3</sub>	No apparent reaction
RhCl <sub>3</sub>	No apparent reaction
PdCl <sub>2</sub>	A very dense, yellow amorphous precipitate forms immediately
Na <sub>2</sub> OsCl <sub>6</sub>	A dense mass of long, yellow, slender, needle-shaped crystals form immediately. These develop small branches along the side and occur singly and in clusters
IrCl <sub>4</sub>	A brown precipitate consisting of a mass of very small clusters and bundles of delicate hair-like crystals form immediately. No definite crystalline form can be recognized
H <sub>2</sub> PtCl <sub>6</sub>	A dense, yellow precipitate forms immediately. This consists of a mass of small radiating clusters of small slender prisms
AuCl <sub>3</sub>	A dense, yellow amorphous precipitate forms immediately

**Detection of bismuth.** Many organic bases, including cinchonine, form insoluble, and in some instances, colored double iodides of the general formula BiI<sub>3</sub>·base·HI with weakly acid solutions of bismuth salts and potassium iodide. Cinchonine iodide-bismuth iodide is orange-red in color. Leger <sup>1,2</sup> was the first to recommend cinchonine as a reagent for the detection of bismuth. More recently Moser,<sup>3</sup> Gutzeit,<sup>4</sup> Feigl and Neuber,<sup>5</sup> and others <sup>6-8,36,37,39</sup> have studied this reaction and report that, although the test is extremely sensitive, it can be used for the detection of bismuth only when no interfering ions are present. The test is carried out as follows:

**Reagent.** Mix 1 g. of cinchonine with 100 ml. of water which has been acidified with a little nitric acid, and warm until the alkaloid is dissolved. Allow the mixture to cool and add 2 g. of potassium iodide.

**Procedure.** Impregnate a strip of filter paper with the cinchonine solution and add a drop of a slightly acid solution to be tested. An orange-red spot forms if bismuth is present. This reaction serves to detect as little as 0.14γ of bismuth at a concentration of 1:350,000.

Lead, copper and mercury salts interfere with this test, owing to the reaction of these cations with the potassium iodide which is present in the test solution. Feigl and Neuber <sup>5</sup> have proposed a method whereby bismuth can be detected in the presence of these ions by making use of the fact that the different metal salts diffuse at different rates through the capillaries of the filter paper, and are therefore fixed in different zones. When a drop of a test solution containing bismuth, copper, mercury and lead is placed upon a filter paper impregnated with the cinchonine reagent, the following zones are observed:

- (a) A white central ring caused by mercury.
- (b) An orange-colored ring of the bismuth compound.
- (c) A yellow ring of lead iodide.
- (d) A brown ring of iodine which is formed by the oxidation of the iodide by means of cupric salts.

The sensitiveness of the bismuth reaction is decreased somewhat by the presence of these interfering ions, but the test, nevertheless, shows the presence of very small quantities of bismuth. In the presence of 100 times as much lead, and 170 times as much copper, 12 $\gamma$  of bismuth can be detected. Fifteen  $\gamma$  of bismuth can be detected in the presence of 100 times as much mercury; and 10 $\gamma$  of bismuth can be detected in the presence of copper, mercury and lead, when the latter are present in the ratio of 84:53:30 times as much of these ions as there is bismuth present.

Cinchonine has been used to precipitate bismuth in the presence of lead. Frick and Engemann<sup>9</sup> claim that this method is more rapid than any other that has been employed when the bismuth content is small. The following procedure is used:

**Procedure.** Neutralize the solution to be analyzed with sodium hydroxide until it gives a bluish-red tint with Congo-red, and then add 20 ml. of a 0.7 per cent aqueous solution of the reagent and allow to stand for 30 minutes. Filter and test the filtrate with a little potassium iodide solution. If a red color appears, the solution was too acid. Dissolve the precipitate in nitric acid and detect or determine bismuth by any of the usual methods.

Ficklen, Newell and Pike<sup>10</sup> have made a careful study of the use of cinchonine and potassium iodide for the detection of bismuth, and they report that while the reagent is extremely sensitive, and can be used in the absence of interfering substances, it is not sufficiently specific to be used in the analysis of mixtures which may contain unknown substances.

**Determination of bismuth.** When cinchonine potassium iodide is mixed with a solution of a bismuth salt, the red to orange color formed is proportional in intensity to the amount of bismuth present. The colloiddally dispersed complex is formed by adding the bismuth solution to the reagent. This reaction may be used for the colorimetric estimation of 0.03-0.15 mg. of bismuth.<sup>40</sup>

**Reagent.** Mix 10 g. of cinchonine with sufficient concentrated nitric acid to form a thick paste. Use no more nitric acid than is necessary. Dissolve the paste in water and dilute to about 100 ml. with water. Dissolve separately 20 g. of potassium iodide in 500 ml. of water, and add to the cinchonine solution. Dilute with water to 1 liter, let stand 48 hours, and filter.

This reagent keeps indefinitely in glass, but must be freed from suspended matter by filtration.

**Procedure.** Transfer 3 ml. of the reagent to each of two 50-ml. Nessler tubes, and to one tube add an aliquot of such size as to impart to the mixture

a crimson or orange hue. Dilute to a definite volume. Prepare a duplicate by adding a standard bismuth solution to the second tube and diluting to the same volume as the sample. The duplication must be carried out immediately, since otherwise the colored complex may precipitate.

Okac<sup>11</sup> has used the following modification of the cinchonine reaction as the basis for a colorimetric method for the determination of 1-25% of bismuth.

**Reagents.** *Cinchonine reagent:* Dissolve 1 g. of cinchonine and 4 g. of sulfuric acid in 50 ml. of water.

*Formate-iodide solution:* Dissolve 100 g. of sodium formate, 15 g. of potassium iodide, 2 g. of sodium sulfite, and 2.5 g. of formic acid in 500 ml. of water.

**Procedure.** Evaporate the solution to be analyzed to dryness with nitric acid, and dissolve the residue in 3 ml. of 10 per cent nitric acid. Heat the solution to boiling, cool, and add 5 ml. of the formate-iodide solution. Mix well and add 1 drop of the cinchonine reagent. Shake the mixture with 1 ml. of cyclohexanone, and compare the red color of the cyclohexanone solution with a series of standards similarly prepared from solutions containing known quantities of bismuth nitrate.

Copper salts impart a yellow color to the cyclohexanone solution and diminish the intensity of the red color due to bismuth. Both thallium and lead interfere, but silver, mercury, cadmium, arsenic, cobalt, chromium, iron, antimony, aluminum, zinc, magnesium and calcium are without appreciable affect.

Garino and Catto<sup>12</sup> have based a method for the determination of small quantities of bismuth in copper upon the electrographic imprint method of Glazunow.<sup>13</sup> This method consists in placing a plate or sheet of metal in contact with a sheet of paper impregnated with a solution of a suitable salt, placing the paper on another sheet of metal, and then connecting the two to a source of direct current. The structure of the metal acting as anode is reproduced on the paper. Bismuth is determined by this method as follows:

**Procedure.** Mix 1 g. of cinchonine with 60 ml. of water and acidify with hydroiodic acid until a slight precipitate is formed. Filter and dilute the solution to 100 ml. Select a piece of copper to be tested that contains exactly 20 square centimeters and solder a wire to it so that it may be used as an electrode. A piece of sheeting of the same area is impregnated with 10 per cent nitric acid solution to act as a buffer, and is placed on the electrode to prevent the precipitation of cinchonine iodobismuthate from adhering to the copper surface. This would increase the resistance of the cell and consequently would prevent the quantitative precipitation of bismuth. Over this is placed a second sheet impregnated with cinchonine iodide. An aluminum cathode is pressed on to the metal and fabric and a current of 100 m.a. and 4 v. is passed through the cell for 4 minutes. An orange-red imprint is left by bismuth on the sheet, and the color is proportional to the amount of bismuth present.

Differences of 0.002 per cent bismuth are readily distinguished for quantities ranging up to 0.01 per cent. For higher concentrations of bismuth, the period of electrolysis is reduced.

**Detection of antimony.** Caille and Viel<sup>12</sup> have used a number of alkaloïds and basic nitrogenous compounds with potassium iodide for the detection of antimony. Quinoline and antipyrine are commonly used for this purpose, but cinchonine may be substituted for these reagents.<sup>10,12</sup>

**Determination of tungsten.** Various organic reagents have been proposed for the determination of tungsten since Lefort<sup>16</sup> first reported that quinine acetate could be used for the precipitation of this metal. Cremer<sup>17</sup> studied the reaction of cinchonine with tungsten in 1895, but it was not until 1918 that it was first employed in an analytical procedure by Low.<sup>18</sup>

Tungsten is usually determined by first converting to the insoluble tungstic acid, and then igniting to  $WO_3$ . Digestion with nitric acid, or preferably with a mixture of hydrochloric and nitric acids, serves to separate practically all tungsten if ammonium and alkali salts are absent, but in the presence of these salts a little of the tungsten remains in solution. The precipitation of the last traces of tungsten is made possible by the use of a little cinchonine.

It is difficult to precipitate tungstic acid by simply evaporating with a solution of a mineral acid. Sodium tungstate,  $Na_2WO_4$ , unites to a limited extent with free tungstic acid to form an acid tungstate,  $Na_2W_4O_{13}$ , and this compound is not easily decomposed by acids. The acid tungstate is converted to a normal tungstate by heating with ammonium hydroxide, but the acid tungstate may be formed again on the addition of an acid. Cinchonine hydrochloride prevents the formation of the acid tungstate, and also prevents the formation of colloidal solutions upon washing. During the ignition of the tungstic acid residue, all organic matter is destroyed so that the presence of cinchonine in the precipitate does not prevent accurate results.

The following method is used for the precipitation of tungstic acid.

**Procedure.** Treat the material to be analyzed with 20 ml. of concentrated hydrochloric acid, then add 10 ml. of concentrated nitric acid, and carefully evaporate to 10-15 ml. Rinse down the cover-glass and the sides of the container with water, and dilute to about 150 ml. Add 5 ml. of a solution prepared by dissolving 12.5 g. of cinchonine in 100 ml. of 6 N hydrochloric acid, and then heat on a hot plate for at least 30 minutes, stirring occasionally and keeping the temperature just below the boiling point. Allow the precipitate to settle, and decant the mixture through a filter containing pulp formed by digesting ashless filter paper with acid. Wash the precipitate 3 times with a solution prepared by diluting 10 ml. of the cinchonine hydrochloride solution with 1 liter of water. Transfer the precipitate to the filter, and wash until free from alkalis. Ignite in an open crucible and weigh as  $WO_3$ .

A number of methods employing cinchonine have been proposed for the determination of tungsten in ores.<sup>19-24</sup> The following procedure has been recommended by Holliday.<sup>25</sup>

**Procedure.** Place 1 g. of the finely ground ore in a 400-ml. beaker, moisten with 5 ml. of water, and add 100 ml. of concentrated hydrochloric acid. Cover the beaker, and heat at about 60° C. for at least 1 hour. Stir the mixture

from time to time with a stirring rod, and evaporate slowly to about 50 ml. Add 40 ml. of concentrated hydrochloric acid and 20 ml. of concentrated nitric acid, and evaporate to about 10 ml. The mixture should be stirred occasionally during the various heating periods. Wash down the cover-glass and sides of the beaker, and dilute the mixture to about 150 ml. Add 5 ml. of a solution prepared by dissolving 12.5 g. of cinchonine in 100 ml. of 6 N hydrochloric acid, and heat the mixture on a hot plate for 30-45 minutes. Keep the temperature of the solution just below the boiling point, and stir from time to time.

Allow the precipitate to settle and decant the mixture through a filter which contains a little paper pulp prepared by digesting ashless filter paper with acid. Wash the precipitate 3 times with a solution containing 10 ml. of the cinchonine hydrochloride solution in 1 liter of hot water. Transfer the precipitate completely to the filter, and wash with the diluted cinchonine hydrochloride solution. With the aid of a jet of water, transfer the precipitate back to the beaker in which the precipitation was carried out. Use about 25 ml. of water for this purpose. Add 6 ml. of concentrated ammonium hydroxide solution, cover the beaker with a watch glass, and heat gently for about 10 minutes to convert the tungstic acid into ammonium tungstate. Rinse the sides of the beaker with a hot, dilute solution prepared by mixing 200 ml. of ammonium hydroxide, 800 ml. of water and 10 ml. of concentrated hydrochloric acid. Stir well and filter through the same filter which was used in the previous filtration. Collect the filtrate in a 400-ml. beaker, and wash the original beaker and the filter with the hot ammoniacal ammonium chloride solution.

The residue on the filter may still contain some tungsten and should be tested in the following manner to insure the complete removal of tungsten: Ignite the residue in an iron crucible and fuse the ash with a little sodium peroxide and sodium carbonate. Extract the melt with water and filter. Acidify the aqueous extract with hydrochloric acid, add 5 ml. of the cinchonine hydrochloride solution, and heat for several hours. If any tungsten remains in the residue, a yellow precipitate of  $\text{WO}_3$  is formed.

Remove the ammonium salts from the filtrate by evaporation and add 20 ml. of concentrated hydrochloric acid and 10 ml. of concentrated nitric acid, and evaporate the solution to a volume of approximately 15 ml. Dilute with 150 ml. of water, and precipitate the last traces of the tungstic acid by treating with the cinchonine solution as described above.

Filter and wash the precipitate as described above, and ignite carefully in a weighed platinum crucible. After burning off the carbon at as low a temperature as possible weigh the precipitate and correct for silica by the usual treatment with hydrofluoric acid.

After the silica is removed, heat the residue to dull redness for only about 1 minute. If tungstic acid is heated over the full flame of a burner, some loss results due to volatilization. The ignited tungsten trioxide should have a clear, lemon-yellow color.

The following rapid method for determining tungsten in ores is recommended by Ledoux: <sup>26</sup>

**Procedure.** Place 1 g. of the ore in a platinum dish, and add 10 ml. of hydrogen fluoride, 25 ml. of concentrated hydrochloric acid, and 10 ml. of 9 N perchloric acid. Heat carefully until the sample is decomposed, adding more hydrofluoric acid if necessary. Evaporate the mixture on an air-bath until fumes of perchloric acid appear, and then dilute with water and transfer to a 400-ml. beaker. Remove any stain which adheres to the platinum dish with a little concentrated ammonium hydroxide and add to the acid solution. To this mixture add 75 ml. of concentrated hydrochloric acid and 25 ml. of concentrated nitric acid, and heat to a temperature slightly below the boiling point. Keep at this temperature until the volume is reduced to about 20 ml. Dilute with 100 ml. of cold water, and add 10 ml. of a solution prepared by dissolving 12.5 g. of cinchonine in 100 ml. of 6 N hydrochloric acid. Allow the mixture to stand for 2 hours, filter, and wash with a solution prepared by diluting 10 ml. of the cinchonine solution to 1 liter. Ignite the residue in a weighed platinum crucible to a dull red heat and weigh. Remove silica by treatment with hydrogen fluoride, and correct for the weight of silica present.

Wilson and Fields <sup>42</sup> have used cinchonine for the determination of traces of tungsten in rocks.

The following method has been used by Rohm <sup>27</sup> for the rapid determination of tungsten in steel:

**Procedure.** Dissolve 5 g. of borings in 90 ml. of 5 N nitric acid, and when solution is complete, add 20 ml. of 1 N potassium permanganate. Boil for a few minutes. Add 0.33 N sodium nitrite solution carefully until the solution is clear, and then add a little paper pulp, 100 ml. of boiling water, 30 ml. of concentrated hydrochloric acid, and 15 ml. of a solution prepared by dissolving 7.5 g. of cinchonine in 100 ml. of 6 N hydrochloric acid. Boil for 5 minutes and filter with suction. Wash with a solution prepared from 900 ml. of water, 35 ml. of concentrated hydrochloric acid, and 15 ml. of the cinchonine reagent. Ignite and weigh as  $WO_3$ .

This method cannot be used for steels which are high in chromium, nor for most of the high-speed steels.

The following method for the determination of tungsten in chrome-tungsten steel is recommended by the National Bureau of Standards:

**Procedure.** Dissolve 1-2 g. of the steel to be analyzed in 50 ml. of 6 N hydrochloric acid, and add 2 ml. of concentrated nitric acid to oxidize iron and tungsten. Heat the mixture until the tungstic acid is bright yellow in color, and dilute to 150 ml. Add 5 ml. of a solution prepared by dissolving 12.5 g. of cinchonine in 100 ml. of 6 N hydrochloric acid. Heat at 90-95° C. for about 30-45 minutes with occasional stirring and filter.

Allow the precipitate to settle, and decant the solution through a filter containing a little paper pulp prepared by digesting ashless filter paper with acid. Wash the precipitate 3 times with a solution prepared by diluting 10 ml. of the cinchonine solution to 1 liter. Ignite the precipitate gently in a platinum

crucible until the carbon is completely oxidized, and treat with a few drops of dilute sulfuric acid and a few ml. of hydrofluoric acid. Evaporate, ignite at a temperature not exceeding  $800^{\circ}\text{C}.$ , and weigh.

Fuse the impure tungstic acid with sodium carbonate, dissolve the melt in water, filter off the precipitate of ferric oxide and chromic oxide, wash thoroughly, transfer to the thoroughly washed crucible and ignite. Repeat the fusion with a small amount of sodium carbonate. Filter, wash, ignite and weigh. Deduct this weight from that of the impure tungstic acid.

Gerke and Kardakova<sup>23</sup> have used a somewhat similar method for the determination of tungsten in hard alloys of the stellite type.

Lambie<sup>30,31,41</sup> claims that the recovery of tungstic oxide from sulfate solutions by treatment with mineral acids or cinchonine is incomplete, and that the method of Schoeller and Jahn<sup>32,38</sup> is more effective. This procedure is as follows:

**Procedure.** Neutralize a solution of an alkali tungstate, which contains some chloride, with dilute hydrochloric acid until neutral to phenolphthalein but basic to methyl orange, and add a freshly prepared solution containing 0.5 g. of tannin in water. Add a little more dilute hydrochloric acid until the solution is acid to litmus, and boil for a few minutes, and then add 5 ml. of a 5 per cent solution of cinchonine hydrochloride that has been diluted somewhat. Boil for an additional 5 minutes and allow to stand for 6 hours. Filter, ignite, and weigh in the usual manner. Use filter paper pulp and wash with a 5 per cent ammonium chloride solution containing a little tannin.

When tungstic acid is precipitated from acid solutions with the aid of cinchonine, high results are obtained in the presence of phosphoric acid. This appears due to the formation of a cinchonine phosphotungstate, which upon ignition yields  $\text{P}_2\text{O}_5 \cdot 24\text{WO}_3$ .<sup>29</sup>

The following method may be used to separate tungstic and phosphoric acids:

**Reagents.** *Cinchonine solution:* Dissolve 50 g. of cinchonine in 500 ml. of 1:1 hydrochloric acid, dilute with water to 1 liter, and filter.

*Wash solution:* Mix 20 ml. of the cinchonine reagent with 100 ml. of 20 per cent ammonium chloride solution and dilute with water to 1 liter.

**Procedure.** To an alkaline solution containing not more than 0.2 g. of tungstic oxide, add 50 ml. of a 20 per cent ammonium chloride solution and dilute to 200 ml. Heat to  $50^{\circ}\text{C}.$  and add 0.5 g. of tannin dissolved in a few ml. of water. Add 6 N hydrochloric acid dropwise with vigorous stirring until the mixture is acid. Add filter paper pulp, and then the cinchonine solution while stirring. Use 5 ml. of the solution for quantities of tungstic oxide ranging up to 0.1 g., and 10 ml. for quantities ranging from 0.1 to 0.2 g. Filter, wash 3 or 4 times with the wash solution, ignite, and weigh as  $\text{WO}_3$ .

**Determination of molybdenum.** If an acid solution containing hexavalent molybdenum is treated with stannous chloride, potassium thiocyanate and cinchonine, a red precipitate is formed which corresponds to the approximate formula  $\text{H}_{33}\text{MoS}_{13}\text{C}_{22}\text{N}_5\text{O}_7$ . This is sometimes referred to as Johnson's molybdenum red. The formation of this compound has been used by Johnson<sup>33</sup> as the basis for a procedure for determining molybdenum in plain and alloy steels.

**Reagents.** *Stannous chloride solution:* Dissolve 250 g. of stannous chloride and 200 ml. of concentrated hydrochloric acid in sufficient water to make 1 liter of solution.

*Cinchonine solution:* Dissolve 12.5 g. of cinchonine in 100 ml. of 6 N hydrochloric acid.

*Wash solution:* Dissolve 10 ml. of the cinchonine solution and 5 g. of ammonium thiocyanate in 500 ml. of water.

**Procedure.** Dissolve 1-2 g. of steel in 4.5 N sulfuric acid and dilute to a volume of 200 ml. Add 20 drops of 30 per cent hydrogen peroxide and boil for 1 minute. Add 100 ml. of water and cool the mixture, and then add 20 ml. of 5 per cent potassium thiocyanate solution, 40 ml. of stannous chloride solution, and 70 ml. of cinchonine solution. Filter, wash the residue with the wash solution, and ignite at lowest red heat in a porcelain crucible. The residue consists of a mixture of  $\text{MoO}_3$ ,  $\text{CuO}$ , and some tin (if the latter two metals are present). Weigh the residue, and extract several times with concentrated ammonia. Always evaporate the  $\text{MoO}_3$  to dryness with 10 drops of concentrated nitric acid before extracting with ammonia. Again ignite the ammonia-insoluble residue, and deduct its weight from that of the first residue. The weight of  $\text{MoO}_3$  and  $\text{CuO}$ , which pass into the ammonia solution, is found by difference. Calculate the weight of  $\text{CuO}$  in the solution by titrating with potassium cyanide, and find the weight of  $\text{MoO}_3$  by difference.

Excellent results were obtained in the analysis of samples containing up to 0.5 per cent of molybdenum, but a slight negative error was observed with quantities of molybdenum ranging as high as 0.9 per cent.

Lelubre<sup>34</sup> recommends the precipitation of molybdenum as lead molybdate or as molybdenum trisulfide, since precipitation with cinchonine involves unnecessary expense.

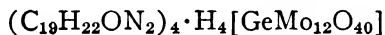
**Detection of molybdenum.** Hammond<sup>43</sup> has used the reaction between molybdenum, stannous chloride, potassium thiocyanate, and cinchonine in a spot test for molybdenum in steel.

**Procedure.** Clean small areas of a blank, a control sample containing 0.15 per cent molybdenum, and the steel to be tested, and brighten with fine sandpaper. Add 1-2 drops of 6 N hydrochloric acid. When the drop of acid begins to bubble vigorously, wait 10 seconds and transfer the liquid to a spot plate. Add 1-2 drops of 25 per cent potassium thiocyanate, and 1-2 drops of a solution prepared by dissolving 3.5 g. of stannous chloride,  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ , in



10 ml. of 1.2 N hydrochloric acid. Then add 2 ml. of a 7 per cent solution of cinchonine in 6 N hydrochloric acid. Allow the mixture to stand overnight. If all cinchonine has dissolved, add a little more of the solid. An orange precipitate forms if molybdenum is present.

**Determination of germanium.** Pyridine has been used for the precipitation of germanium as the germanomolybdate, but according to Davies and Morgan<sup>35</sup> this precipitation is not entirely satisfactory. Other amines, particularly tertiary amines, have been studied with a view of obtaining more insoluble precipitates; but unfortunately when more insoluble germanomolybdates are obtained, molybdenum trioxide is also precipitated. Cinchonine has been recommended as the most satisfactory precipitant for germanomolybdic acid. Cinchonine germanomolybdate forms as a yellow amorphous precipitate, which is not appreciably soluble in dilute ammonium nitrate solutions. When the compound is dried at 160° C. it has the following composition:



The germanium content of this precipitate is 2.385 per cent. The following procedure is used for determining up to 5 mg. of germanium:

**Procedure.** To 40 ml. of a neutral solution of the germanium salt, add 20 ml. of 25 per cent ammonium nitrate solution, 16 ml. of 2 per cent ammonium molybdate solution, and then with stirring, 20 ml. of 2 N nitric acid. Finally add 9 ml. of a 2.5 per cent solution of cinchonine in 0.25 N nitric acid. Allow the mixture to stand for 2-4 hours with occasional stirring. Some experience is required to determine when precipitation is complete, since the supernatant liquid never becomes quite clear, but always retains a faint opalescence. If, however, after stirring and settling for 10 minutes, the opalescence does not increase during the next 30 minutes, the precipitate may be filtered without danger of loss of germanium. Collect the precipitate in a filter crucible, wash with 2.5 per cent ammonium nitrate solution containing 5 ml. of 2 N nitric acid per 100 ml., and dry at 160° C. for 2 hours. The precipitate contains 2.385 per cent germanium.

Results obtained using this method are somewhat low when more than 4 mg. of germanium is present. Results may be made somewhat more accurate under these conditions by using 18 ml. of the molybdate solution and 10 ml. of the reagent solution. It is also advisable that the mixture stand overnight before filtering.

**Detection of cadmium.** A white precipitate is formed when a 3 per cent solution of cinchonine in dilute nitric acid is added to an acid solution of a cadmium salt containing potassium iodide.<sup>7</sup> The sensitivity of this reaction is 1:110,000. Mercury, lead, bismuth, copper and antimony give similar reactions.

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## CINCHOPHEN

Synonym: Phenylcinchoninic acid, 2-phenylquinoline-4-carboxylic acid, atophan, quinophan, phenoquin, agotan

$C_{16}H_{11}O_2N$

Mol. Wt. 249.09

Beil. Ref. XXII, 103(518).



**Use:** Detection of copper, gold, iron, lead, osmium, palladium, platinum, rhodium, ruthenium, silver and zinc.

Cinchophen consists of small white needles or a crystalline powder. It is odorless and slightly bitter. It is insoluble in cold water, but dissolves in ether and dilute alkali hydroxide solutions. One gram of the solid dissolves in about 120 ml. of alcohol or 400 ml. of chloroform. Cinchophen hydrochloride is a yellow crystalline powder, which is slightly bitter and possesses an astringent taste. It melts at about 220° C. It is insoluble in water, slightly soluble in alcohol, but is soluble in chloroform and ether.

**Preparation:** Mix equal molecular quantities of pyruvic acid and benzaldehyde dissolved in alcohol in a flask equipped with a reflux condenser, and add slowly from a dropping funnel a molecular quantity of aniline dissolved in alcohol. Warm for 3 hours on a water-bath. Allow the mixture to cool and collect the crystals which form by filtration. Purify by recrystallizing from dilute alcohol.<sup>1,2</sup>

**Reactions.** Cinchophen reacts with a hot solution of platinic chloride in hydrochloric acid to form a brick-red precipitate of the platinum salt,  $(C_{10}H_{11}NO_2 \cdot HCl)_2 \cdot PtCl_4$ . A white, flocculent silver salt is precipitated from a solution of an ammonium salt. A green flocculent copper salt; a yellow flocculent lead compound; and a white zinc salt are also formed when the reagent is added to solutions containing these ions.

Whitmore and Schneider<sup>3</sup> have studied the use of cinchophen as a microchemical reagent for the detection of platinum metals, and their results are shown in Table 41.

TABLE 41.—REACTION OF CINCHOPEN WITH PLATINUM METALS

Test Material	Description
$RuCl_3$	On standing some very compact clusters of very small, bristle-like structures form around the edge of the drop
$RhCl_3$	On standing a short time a border of very delicate, hair-like crystals, brown in color, forms around the circumference
$PdCl_2$	On standing a short time, rather large, compact clusters of very small, brown, needle-like crystals form around the circumference. Gradually these develop over the entire drop
$Na_2OsCl_6$	A border of very delicate, brown, hair-like crystals develops almost immediately around the edge of the drop. These are similar to the crystals obtained with $RhCl_3$
$IrCl_3$	On standing a short time very compact clusters of small, brown, bristle-like crystals form around the edge of the drop. These gradually develop throughout the drop as it evaporates
$H_2PtCl_6$	Dense, radiating clusters of fine, slender, brown, bristle-like crystals develop gradually around the edge of the drop
$AuCl_3$	A very fine, brownish-yellow, granular precipitate forms immediately. This precipitate changes over very rapidly to a great many small clusters of short, bright-yellow prisms

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**COCAINE**

Synonym: Methylbenzoylecgonine

 $C_{17}H_{21}O_4N$ 

Mol. Wt. 303.17

Beil. Ref. XXII, 198, 206, 211, 212 (547, 548).

**Use:** Detection of antimony, bismuth, chromium, ferricyanide, ferrocyanide, fluorine, iridium, iron, germanium, gold, lead, manganese, osmium, ruthenium, palladium and platinum.

Determination of arsenic, fluorine, and silicon.

Cocaine consists of colorless crystals, or occurs as a white crystalline powder. It melts at 96-98° C. One g. dissolves in 600 ml. of cold water or 270 ml. of water at 80° C.; 6.5 ml. of alcohol; 0.7 ml. of chloroform; and 3.5 ml. of ether. It is also soluble in acetone, ethyl acetate, and carbon disulfide.

**Detection of lead, bismuth and antimony.** A reaction for antimony and bismuth proposed by Caille and Viel,<sup>1</sup> using cocaine and potassium iodide, may be used with suitable modification for the detection of antimony. A yellow amorphous precipitate is formed when 1 ml. of a solution containing cocaine hydrochloride is added to 4 ml. of a cold solution containing 5 g. of antimony trichloride, 20 ml. of concentrated hydrochloric acid, and 40 g. of potassium iodide.

Martini<sup>2</sup> has studied the use of cocaine for the microdetection of lead, bismuth and antimony in minerals. The reverse of the  $K_2PbI_4$  test for alkaloids can be used for the detection of lead, and an analogous test can be used for the other metals. A 5 per cent solution of cocaine and a 5 per cent solution of potassium iodide are used. The sensitivity of the lead test is 0.01 $\gamma$  of lead at a limiting concentration of 1:100,000. Silver and mercuric ions interfere, but lead can be separated from these ions by precipitating as lead sulfate. After dissolving this precipitate in ammonium tartrate, the test may be applied to the resulting solution. If potassium bromide is substituted for potassium iodide, bismuth yields a bright yellow precipitate which is observed with as little as 0.5 $\gamma$  of bismuth. Antimony gives a deep red precipitate, and the reaction has about the same sensitivity as that with bismuth.

**Detection and determination of silicon and fluorine.** Silicon may be determined nephelometrically by a method proposed by Wachsmuth.<sup>3</sup>

**Reagent.** Mix 4.3 ml. of 5 per cent sodium molybdate, 4.3 ml. of 2.5 per cent cocaine hydrochloride, and 11.4 ml. of 96 per cent acetic acid.

**Procedure.** Add 4 ml. of the reagent to 6 ml. of the sample to be analyzed. If silicates are present, a turbidity appears almost instantaneously and it reaches a maximum after 2 or 3 minutes. The opalescence varies with the

quantity of silicon present, and may be used for the estimation of silicates. This reaction serves to detect 0.0005 mg. of silicon in 10 ml. of solution.

This reaction may also be used for the indirect estimation of fluorine after separation as silicon tetrafluoride.

**Determination of arsenic.** Arsenic may also be determined by the opalescence which appears when an acid solution of potassium molybdate and cocaine are added to an almost neutral solution containing arsenic acid.<sup>4,5</sup>

**Reagent.** Mix 1 volume of 1 per cent potassium molybdate solution with 2 volumes of 1 N hydrochloric acid, and then add with continuous shaking 1 volume of a 2 per cent solution of cocaine hydrochloride. Filter through a quantitative filter paper just before using. The reagent may be kept for several weeks.

TABLE 42.—DETECTION OF THE PLATINUM METALS WITH  
COCAINE HYDROCHLORIDE

Test Material	Description
$\text{RuCl}_3$	Many very small pointed crystals form immediately around the test particle. All of these are bent at a slight angle at the mid-point. They occur singly, also as crosses and a few clusters
$\text{RhCl}_3$	No apparent reaction
$\text{PdCl}_2$	A very dense, brown, granular precipitate forms immediately around the test particle
$\text{Na}_2\text{OsCl}_6$	A very dense mass of long, slender crystals of a branching or feather-like form develops immediately around the test particle
$\text{IrCl}_3$	Long crystalline forms, brown in color and of a feather-like form, develop around the reagent particle. At the edge of the drop many deep-red octahedra appear.
$\text{H}_2\text{PtCl}_6$	A very dense mass of feather-like crystals develops immediately around the reagent particle. This precipitate is so dense that no typical forms can be recognized
$\text{AuCl}_3$	A very dense, yellow, granular precipitate forms immediately. On long standing, branching clusters of feather-like forms develop throughout this precipitate

**Procedure.** Treat the desired volume of solution containing arsenic acid with an equal volume of the clear filtered reagent. When using the Kleinmann macronephelometer, the volume of solution taken must be at least 7.5 ml. The amount of arsenic contained in this volume may range from 0.06 to 0.0025 mg. With the Kleinmann micronephelometer, for which a total volume of only 5 ml. is necessary, use 2.5 ml. of the test solution. This may contain as little as 0.0005 mg. of arsenic. The arsenic solution and the reagent are best mixed in a small glass-stoppered flask. The reagent should be added to the unknown and to the standard solution as nearly at the same time as possible. The standard solution should be selected such that it has as nearly as possible the same concentration as the unknown. Mixtures containing down to 0.01 mg. of arsenic

acid in the final volume of 15 ml. are allowed to stand 20 minutes before measuring. With less than 0.01 mg. of arsenic acid in the same volume, allow the mixture to stand for 30 minutes. Measurements may be made with an accuracy of 2-3 per cent with quantities of arsenic greater than 0.005 mg. With less than 0.005 mg. of arsenic the accuracy is about 5 per cent.

**Detection of germanium.** A white precipitate is formed when a solution of  $\text{Ge}(\text{OH})_2$  in hydroiodic acid is treated with an aqueous solution of cocaine hydrochloride. This precipitate consists of  $3(\text{C}_{17}\text{H}_{21}\text{NO}_4 \cdot \text{HI}) \cdot 2\text{GeI}_2$ . This reaction may be used for the detection of germanium.<sup>7</sup>

**Detection of the platinum metals.** Whitmore and Schneider<sup>6</sup> have investigated the use of cocaine hydrochloride as a microchemical reagent for the detection of the platinum metals. The results obtained by adding a crystal of cocaine hydrochloride to solutions of various salts of the platinum metals are given in Table 42.

**Microchemical reactions.** Cocaine forms crystalline precipitates with chromate, ferrocyanide, ferricyanide, permanganate, ferric chloride, platonic chloride, auric chloride which can be used for the microchemical detection of these substances.<sup>8</sup>

1. M. Caille and E. Viel, *Compt. rend.* **176**, 1156-9 (1923); *C.A.* **17**, 2289 (1923).
2. A. Martini, *Pub. inst. investigaciones microquim. Univ. nacl. litoral (Rosario, Argentina)*, **4**, 41-4 (1940); *C.A.* **36**, 367 (1942).
3. H. Wachsmuth, *J. pharm. Belg.* **19**, 575-7; 609, 627, 627-31 (1937); *C.A.* **31**, 8419 (1937).
4. H. Kleinmann and F. Pangritz, *Biochem. Z.* **185**, 14-43 (1927); *C.A.* **21**, 3853 (1927).
5. H. Kleinmann, *Deut. Z. ges. gericht. Med.* **11**, 61-71 (1928); *C.A.* **22**, 1743 (1928).
6. W. F. Whitmore and H. Schneider, *Mikrochemie.* **17**, 279-319 (1935).
7. T. Karantassis and L. Capatos, *Compt. rend.* **201**, 74-5 (1935).
8. M. Wagenaar, *Pharm. Weekblad.* **67**, 229-32 (1930).

## CODEINE

Synonym: Methylmorphine

$\text{C}_{18}\text{H}_{21}\text{O}_3 \cdot \text{N} \cdot \text{H}_2\text{O}$

Mol. Wt. 317.19

**Use:** Detection and determination of selenium, and detection of oxidizing agents.

The alkaloid codeine is a colorless, odorless, crystalline solid, which melts at  $154^\circ$ - $156^\circ$  C. Its aqueous solution is strongly alkaline. One g. of the alkaloid dissolves in 120 ml. of water, 60 ml. of hot water, 2 ml. of alcohol, 13 ml. benzene, 18 ml. of ether and 0.5 ml. of chloroform. It is freely soluble in amyl alcohol, methyl alcohol, and dilute acids, but it is insoluble in solutions of alkali hydroxides.

**Detection of selenium.** Sulfuric acid containing only 0.0001 per cent of selenious acid yields with 0.01 g. of codeine phosphate a green or bluish-green color.<sup>1,9,10</sup> The test is not successful if the sulfuric acid contains considerable iron.<sup>1</sup>

Stover and Hopkins <sup>7</sup> have used a similar reaction for the detection of selenium in plants. In this process the sample is decomposed by heating with nitric acid and sulfuric acid before applying the codeine test. Horn <sup>8</sup> points out that this method is open to several criticisms: (a) there is a possibility of loss of selenium by heating with nitric acid; (b) it is difficult to remove all nitric acid (an essential step); and (c) the method is time consuming. The following method is recommended:

**Procedure.** Place 1 g. of the sample in a Kjeldahl flask and add 40 ml. of concentrated sulfuric acid and 0.2 g. of mercuric oxide. Heat until the mixture is colorless, and then cool. Dilute to a definite volume with concentrated sulfuric acid. Transfer 5 ml. of the cooled mixture to a test tube and add 2 drops of a 3 per cent codeine sulfate solution. Cool and shake after the addition of each drop. A green color forms and rapidly changes to blue if selenium is present.

Schmidt <sup>1</sup> has shown that 1 drop of concentrated ferric chloride in 10 ml. of concentrated sulfuric acid interferes. Vanadium also interferes. Nitric acid causes a red color. If the digested sample is allowed to stand in air for a time, sufficient moisture is absorbed to interfere by preventing color formation. The reagent should be added as soon as possible after cooling.

**Determination of selenium.** A reaction similar to that described above may be used for the colorimetric determination of selenium dioxide in sulfuric acid.<sup>2</sup>

**Procedure.** Add 0.1 ml. of a 4 per cent aqueous solution of codeine phosphate to 10 ml. of a solution of selenium dioxide in concentrated sulfuric acid. A convenient depth of color for comparison is obtained in concentrations of selenium dioxide ranging from 0.01 per cent to 0.00005 per cent.

Arsenic acid gives no perceptible coloration when present in concentrations less than 1 per cent. Ferric salts give a blue coloration, but of a hue different from that produced with selenium dioxide. The color with ferric salts is obtained when the iron content of the mixture exceeds 0.0015 per cent. In the presence of phosphoric acid the color appears only when the concentration of iron is greater than 0.0074 per cent.

While studying the quantitative adaptation of the codeine reaction to the colorimetric determination of selenium in plant materials, Davidson <sup>3</sup> found that the presence of iron is essential for the development of a relatively stable and lasting color. This method gives consistent results in recovering selenium which has been added to wheat. The results compare favorably with those obtained by the method of Robinson and co-workers.<sup>4</sup>

Lindhe <sup>5</sup> has used the codeine reaction for determining selenium in sulfur.

**Procedure.** Dissolve 1-10 g. of sulfur in fuming nitric acid, add 10 ml. of concentrated sulfuric acid, and evaporate until the mixture fumes. Cool, wash down the walls of the vessel with water, again evaporate until the mixture fumes, and transfer to a 50-ml. graduate having a glass stopper. Dilute with

concentrated sulfuric acid to 20 ml. if a 1 g. sample was used, or to 50 ml. if the sample weighed 10 g. Then add 10-50 mg. of codeine sulfate and shake. If much selenium is present, a clear green color is obtained, and this gradually changes to blue. Small quantities of selenium give a blue color immediately. Compare the color of this solution with that of standards similarly prepared.

Organic impurities and ferric salts in sulfuric acid interfere with this reaction.

**Detection of oxidizing agents.** Pesetz <sup>6</sup> has used a modification of Husemann's color test of the opium alkaloids for the detection of oxidizing agents.

**Procedure.** Dissolve several mg. of codeine or its salt in 0.5 ml. of 90-95 per cent alcohol, and boil the solution on a steam bath for 2-3 minutes with 1.5 ml. of concentrated sulfuric acid. Cool the mixture and carefully dilute with 5 ml. of water. Divide the solution into three parts.

(a) To one part of the above reagent add 1-2 drops sodium hypochlorite solution. A red-orange solution is obtained which shows an absorption band in the bluish-violet region of the spectrum, and this is not eliminated by the addition of stannous chloride.

(b) A similar color is obtained with bromine water.

(c) A similar color is also obtained with 1 per cent sodium nitrite solution.

A colorless solution obtained by adding 20 ml. of water to a cold mixture of 1 ml. of a 5 per cent alcoholic solution of codeine and 2 ml. of concentrated sulfuric acid has been used to detect bromine in dilutions of 0.02 g. per liter, or of nitrous acid or nitrites in solutions containing only 0.01 g. per liter. This reagent also gives positive reactions with 0.5 per cent solutions of chlorine or hypochlorites, but no reaction is obtained with nitric acid, nitrates, chlorates, persulfates, peroxides and hydrogen peroxide.

1. E. Schmidt, *Arch. Pharm.* **252**, 161-5 (1914); *C.A.* **8**, 2990 (1914).
2. T. Raikhinstein, *Trans. Inst. Pure Chem. Reagents (Moscow)*. No. 6, 27-30 (1927); *C.A.* **23**, 2391 (1929).
3. J. Davidson, *J. Assoc. Official Agr. Chem.* **22**, 450-8 (1939); *C.A.* **33**, 7237 (1939).
4. W. O. Robinson, H. C. Dudley, K. T. Williams, and H. G. Beyers, *Ind. Eng. Chem., Anal. Ed.* **6**, 274-6 (1934); *C.A.* **28**, 5363 (1934).
5. H. Lindhe, *Iva.* **2**, 42-3 (1936); *C.A.* **30**, 4783 (1936).
6. M. Pesetz, *Bull. soc. chim.* [5] **3**, 675-6 (1936); *C.A.* **30**, 4433 (1936).
7. N. M. Stover and B. S. Hopkins, *Ind. Eng. Chem.* **19**, 510 (1927).
8. M. J. Horn, *Ind. Eng. Chem., Anal. Ed.* **6**, 34-5 (1934).
9. R. Fritsch, *Z. physiol. Chem.* **104**, 59 (1918); *C.A.* **13**, 2047 (1919).
10. E. J. C. Bowmaker and J. D. Cauwood, *J. Soc. Glass Tech.* **11**, 386 (1927); *C.A.* **22**, 1440 (1928).

## COLCHICINE

$C_{22}H_{25}ON_6$

Mol. Wt. 399.20

**Use:** Detection of selenium.

Colchicine consists of pale yellow, odorless, amorphous scales of powder. It has a bitter taste, and darkens on exposure to light. It is very poisonous. The



melting point is 145° C. One gram of the alkaloid dissolves in 22 ml. of water; 220 ml. of ether, and 100 ml. of benzene. It is freely soluble in alcohol and chloroform. This alkaloid forms no salts with the mineral acids.

**Detection of selenium.** Selenium may be detected by the yellow color which it forms with colchicine.<sup>1</sup>

1. R. Fritsch, *Z. physiol. Chem.* **104**, 59 (1918); *C.A.* **13**, 2047 (1919).

## CONIINE

$C_8H_{17}N$

Mol. Wt. 127.14

Beil. Ref. XX, 110, 118, 119 (30, 31).

**Use:** Detection of silicon.

This reagent is a colorless, oily liquid. It darkens with age and with exposure to light. It is *very poisonous*. It is a strong base and is volatile with steam. It melts at -2° C., boils at 166-167° C., and has a sp. gr. of 0.845. It is soluble in 100 parts of water, but is less soluble in hot water. It is miscible with alcohol, soluble in benzene, ether, amyl alcohol, acetone, dilute acids, and is sparingly soluble in chloroform.

**Determination of silicon.** In acid solutions, silicic acid reacts with ammonium molybdate to give a precipitate containing 3 moles of ammonia, 1 mole silicon dioxide, and 12 moles of molybdic oxide. The formation of this compound has been used for detecting small quantities of dissolved silicic acid. The silicomolybdic acid forms insoluble salts with organic bases. Coniine has been used for this purpose.<sup>1</sup>

1. E. J. King and J. L. Watson, *Mikrochemie.* **20**, 49-56 (1936); *C.A.* **30**, 5151 (1936).

## DIACETYLMORPHINE

Synonym: Heroin, diamorphine

$H_{21}H_{23}O_5N$

Mol. Wt. 369.19

**Use:** Detection of copper.

Diacetylmorphine is a white, bitter crystalline compound. It melts at 172° C. It is almost insoluble in water but is moderately soluble in alcohol and ether.

**Detection of copper:** Copper is detected by the following method which has been proposed by Fulton:<sup>1</sup>

**Procedure.** To 3 ml. of an aqueous solution of diacetylmorphine, add 0.5 ml. of hydrogen peroxide and 0.5 ml. of 5 N ammonium hydroxide. Then add the solution containing the copper salt. A pink or red color appears if copper is present.

1. C. C. Fulton, *Am. J. Pharm.* **105**, 25 (1933).

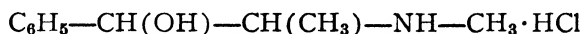
**EPHEDRINE HYDROCHLORIDE**

Synonym: 1, Phenyl-2-methylaminopropanol hydrochloride

 $C_{10}H_{15}ON \cdot HCl$ 

Mol. Wt. 201.79

Beil. Ref. XIII, 636.

**Use:** Detection of osmium.

Ephedrine hydrochloride is a white crystalline solid melting at 216-220° C. It is soluble in water and somewhat less soluble in alcohol. It is insoluble in ether.

**Detection of osmium.** An orange color is formed when a drop of a saturated aqueous solution of ephedrine hydrochloride is added to a solution of sodium osmate that has been made alkaline with sodium hydroxide. The test is made more sensitive by extracting the colored solution with carbon tetrachloride. The color of the carbon tetrachloride layer is amber yellow.

1. S. O. Thompson, F. E. Beamish and M. Scott, *Ind. Eng. Chem., Anal. Ed.* **9**, 421 (1937).

**ESPARTINE**

Synonym: Sparteine, lupinidine

 $C_{15}H_{26}N_2$ 

Mol. Wt. 234.22

**Use:** Detection of antimony, cobalt, gold, iron, osmium, palladium and uranium.

Espartine is a colorless, oily, very bitter liquid having a strongly basic reaction. It boils at 326° C., and it has a sp. gr. of 1.027. It is slightly soluble in water, but it is soluble in alcohol, chloroform, and ether.

**Detection of iron and cobalt.** A concentrated solution of cobalt thiocyanate reacts with a solution of espartine to yield a blue precipitate, which shows strong double refraction in a polarizing microscope with crossed Nichols, and the same color with parallel Nichols. This is a very sensitive reaction for the alkaloid. This reaction has also been used by Martini<sup>1,2</sup> as a very sensitive test for cobalt, and also for ferric salts with which it yields a red color.

**Reagent.** Dissolve 40 g. of ammonium thiocyanate and 5 g. of espartine in 100 ml. of water.

**Procedure.** Add a little 20 per cent hydrogen peroxide to a drop of 0.1 per cent ferric chloride solution, and then add 1 drop of the espartine-ammonium thiocyanate reagent and stir. A red precipitate is formed, which under high magnification appears as acicular crystals grouped in bundles.

A similar test with 0.1 per cent cobalt chloride solution yields blue, rectangular, tabular crystals grouped in rosettes. With zinc, the espartine-ammonium thiocyanate reagent yields white crystals; and with vanadium, small prismatic wine red crystals are obtained. In dilute solutions containing iron, together with cobalt, nickel, zinc, cadmium or copper, in which the quantity of the other ion

does not exceed that of the iron by more than 100-fold, characteristic crystals of the iron compound may readily be observed.

Morello<sup>3</sup> has used the reagent of Martini for the detection of iron in plants. This reaction not only shows the presence of iron in plants, but it also shows its exact distribution. This test is made as follows:

**Procedure.** Place 1 N hydrochloric acid, perhydrol, and espartine solution successively on a microscope slide; and, if no color is observed, add a section of the plant which has been prepared without the aid of steel implements.

**Detection of uranium, gold, and antimony.** Martini<sup>4</sup> has used the espartine-thiocyanate reagent as a sensitive test for uranium. As little as 0.1γ of this element can be detected in this way. As little as 0.1γ of gold can also be detected by a similar reaction.

Caille and Viel<sup>6</sup> have used espartine like other nitrogenous compounds, with potassium iodide as a sensitive test for antimony.

**Reactions with the platinum metals.** Whitmore and Schneider<sup>7</sup> have studied the use of espartine as a reagent for the platinum metals. Table 43, taken from their publication, shows the results obtained when a 1 per cent solution of espartine sulfate is added to 2 per cent solutions of the materials to be tested:

TABLE 43.—REACTIONS OF ESPARTINE WITH THE PLATINUM METALS

Test Material	Description
RuCl <sub>3</sub>	No apparent reaction
RhCl <sub>3</sub>	No apparent reaction
PdCl <sub>2</sub>	On standing a short time many, very irregular, quite large, bright yellow granules appear. These seem to be made up of a compact mass of very small crystals. No distinct form can be recognized.
Na <sub>2</sub> OsCl <sub>6</sub>	On standing and as the drop evaporates a border of very small, irregular, bright yellow crystals develops around the circumference. Among these some very small hexagonal plates can be distinguished
IrCl <sub>3</sub>	No apparent reaction
H <sub>2</sub> PtCl <sub>6</sub>	A yellow, granular precipitate forms immediately
AuCl <sub>3</sub>	A very dense, yellow, granular precipitate forms immediately. This precipitate gradually changes over to a great many bright-yellow crystals. These appear to be short hexagonal prisms. Many irregular clusters also appear

1. A. Martini, *Anales asoc. quim. Argentina*, **24**, 168 (1936); *C.A.* **31**, 5709 (1937).
2. A. Martini, *Mikrochim. Acta*, **1**, 164-7 (1937); *C.A.* **31**, 7797 (1937).
3. M. A. Morello, *Mikrochemie ver. Mikrochim. Acta*, **28**, 245-53 (1940); *C.A.* **36**, 367 (1942).
4. A. Martini, *Anales asoc. quim. Argentina*, **30**, 41 (1942); *C.A.* **36**, 5723 (1942).
5. A. Martini, *Pub. inst. investigaciones, Univ. nacl. litoral*, **3**, 75-93 (1939); *C.A.* **36**, 6105 (1942).
6. M. Caille and E. Viel, *Compt. rend.* **176**, 1156-9 (1923); *C.A.* **17**, 2289 (1923).
7. W. F. Whitmore and H. Schneider, *Mikrochemie*, **17**, 279-319 (1935).

**ETHYLMORPHINE** $C_{19}H_{24}O_3NCl \cdot 2H_2O$ 

Mol. Wt. 385.68

**Use:** Detection of arsenate.

Ethylmorphine hydrochloride is a white crystalline powder. The dihydrate melts at about 123° C. with decomposition, and the anhydrous compound melts at about 170° C. with decomposition. The compound is moderately soluble in water and alcohol, but is only slightly soluble in chloroform and ether.

**Detection of arsenate.** A sulfuric acid solution of ethylmorphine reacts with sodium arsenate on gentle warming to give a dark blue color.<sup>1</sup>

1. L. Ekkert, *Pharm. Zentralhalle*. **75**, 49, 50 (1934).

**HYDROSTRYCHNINE**

This reagent, which is formed by the reduction of strychnine, is used in a number of analytical procedures. A discussion of the uses of this compound is included in the section on strychnine.

**HYOSCINE HYDROCHLORIDE**

Synonym: Scopalamine hydrochloride

 $C_{17}H_{21}O_4N \cdot HCl$ 

Mol. Wt. 375.67

Beil. Ref. XXVII, 99, 102.

**Use:** Detection of gold.

The free alkaloid is obtained as an almost colorless syrupy liquid from its chloroform solution, but it may be crystallized from ether. The hydrochloride consists of white crystals which are soluble in water.

**Detection of gold.** When a solution of hyoscine hydrochloride is added to an aqueous solution of gold chloride, a light yellow, amorphous precipitate forms immediately. This changes almost at once to a mass of long yellow branching crystals. Other metals of the platinum group give no tests with this reagent.<sup>1</sup>

1. W. F. Whitmore and H. Schneider, *Mikrochemie*. **17**, 279-319 (1935).

**HYOSCYAMINE** $C_{17}H_{23}O_3N$ 

Mol. Wt. 289.19

Beil. Ref. XXI, 24(198).

**Use:** Detection of gold.

Hyoscyamine is isomeric with atropine, and is identical with daturine. It is very poisonous and consists of white crystals, which melt at 107-108.5° C. It is only very slightly soluble in water, more so in ether and benzene, but is fairly soluble in chloroform, and is freely soluble in alcohol and dilute acids.

**Detection of gold.** A dense, pale-yellow precipitate forms immediately when a solution of hyosycamine is added to a solution of gold chloride. The

precipitate changes rapidly into pale-yellow, rectangular plates. This reaction may be used for the microchemical detection of gold. Other metals of the platinum group do not yield test forms with hyoscyamine, but the gold test is not satisfactory in the presence of other elements of this group.

1. W. F. Whitmore and H. Schneider, *Mikrochemie*, 17, 279-319 (1935).

## MORPHINE

$C_{17}H_{19}O_3N \cdot H_2O$

Mol. Wt. 303.17

Beil. Ref. XXVII, 131.

**Use:** Detection of antimony, cerium, copper, columbium, erbium, perchlorate, praseodymium, silica, tantalum, titanium, tungsten, and zirconium.

Morphine is the most important alkaloid in opium. It consists of white lustrous prisms or fine needles, or a crystalline powder having a bitter taste. It darkens on exposure to light and becomes anhydrous at  $110^\circ\text{C}$ . It is odorless and poisonous. It melts at about  $230^\circ\text{C}$ . with decomposition, and when anhydrous melts at  $254^\circ\text{C}$ . with decomposition. One gram of the alkaloid dissolves in 5 liters of cold water, 1100 ml. of boiling water, 210 ml. of alcohol, 98 ml. of boiling alcohol, 1200 ml. of chloroform, 6250 ml. of ether, 10 ml. of boiling methyl alcohol. It is quite soluble in solutions of sodium and potassium hydroxides. It is insoluble in benzene. The aqueous solution has a pH of about 8.

Morphine hydrochloride, which is commonly used as the analytical reagent, consists of white flakes or crystalline powder having a bitter taste. It melts at about  $200^\circ\text{C}$ . with decomposition. One g. of the salt dissolves in 17.5 ml. of water, 0.5 ml. of boiling water, 52 ml. of alcohol, and 6 ml. of alcohol at  $60^\circ\text{C}$ . It is insoluble in chloroform and ether.

**Detection of cerium.** Cerous and ceric salts react with morphine hydrochloride in an ammoniacal solution to form a light or dark chocolate-colored precipitate. This reaction is explained as due to the fact that the morphine molecule contains hydroxyl groups and acts as a polyphenol. No color reaction is obtained with lanthanum or thorium in an ammoniacal solution, nor with cerium, lanthanum or thorium in acid or neutral solutions. This reaction has been used by Shemyakin<sup>1</sup> for the detection of cerium.

**Procedure.** Add a few grains of morphine hydrochloride and a few drops of ammonium hydroxide to a solution containing a cerium salt. A chocolate-colored precipitate is obtained if cerium is present.

This test is modified by adding a 0.1-1.0 per cent solution of morphine hydrochloride to a 0.00001-0.01 M solution of ceric sulfate or cerous nitrate, and then treating dropwise with a 25 per cent solution of ammonium hydroxide. A chocolate-colored precipitate indicates the presence of cerium.

Cerium may also be detected by using the so-called "brown ring method":

**Procedure.** To a mixture of solutions of morphine hydrochloride and cerium salts contained in a glass cylinder about 200 mm. in height and having an inside diameter of 8 mm., carefully add a layer of ammonium hydroxide so

as to insure the formation of a sharply defined boundary between the two layers. When the ammonium hydroxide begins to diffuse into the morphine-cerium salt mixture, the resulting precipitate forms as a clearly marked brown ring at the boundary between the two liquids. This is visible at cerium concentrations as low as 0.02-0.002 mg. of cerium per ml.

Cerium may also be detected with morphine by means of a spot test.

**Procedure.** Impregnate filter paper with a 0.1-1.0 per cent morphine hydrochloride solution, and add a drop of the solution to be tested. Then expose the resulting mixture to the vapors of ammonia, or add a drop of a 25 per cent ammonium hydroxide solution. The brown stain which appears if cerium is present is very distinct at concentrations as low as 0.04 mg. of cerium per ml., and is still visible at concentrations as low as 0.001 mg. per ml.

If potassium hydroxide is used in place of ammonium hydroxide, the stain is much less distinct with trivalent than with tetravalent cerium, and appears much more slowly.

**Reactions with the rare earths.** Shemyakin<sup>2</sup> has studied the reaction of morphine hydrochloride with praseodymium, dysprosium, erbium, yttrium, thorium and lanthanum. When the alkaloid is added to praseodymium or dysprosium nitrate in an ammoniacal solution, a color reaction is obtained only on long standing. Erbium nitrate in a neutral or ammoniacal solution gives a precipitate of white needle-like crystals on treatment with morphine hydrochloride. Yttrium nitrate or titanium sulfate reacts similarly. A white precipitate is obtained with zirconium nitrate. A fine white precipitate is obtained when morphine hydrochloride is added to a solution of  $K_2CfF_7$  or  $K_2TaF_7$ . Iron, chromium, aluminum, manganese, nickel, cobalt and zinc give no reaction with morphine hydrochloride.<sup>3</sup>

**Reactions with tantalum, tungsten and titanium.** Moir<sup>11</sup> and Levy<sup>12-14</sup> have investigated the reactions of morphine and other alkaloids on columbium and tantalum. The reaction is carried out in concentrated sulfuric acid.

Hall and Smith<sup>4,5</sup> have studied the reaction of morphine with the double fluorides of tantalum, tungsten and titanium, and report that only titanium gives a satisfactory reaction.

**Procedure.** Dissolve a little morphine in 8-10 drops of concentrated sulfuric acid on a glazed porcelain plate, and add a crystal of the double fluoride of tantalum, tungsten or titanium. With tantalum a faint yellow color is obtained; with tungsten a very delicate red to brown coloration; and with titanium a gray-brown color appears, which eventually becomes purple.

LaCroix<sup>6</sup> has used morphine to detect titanium. On adding a drop of a solution containing a titanium salt to a solution of morphine in concentrated sulfuric acid, a wine-red color immediately develops.

**Detection of copper.** Fulton<sup>7</sup> has used morphine sulfate as a very sensitive reaction for copper.

**Procedure.** Dissolve 0.03 g. of morphine sulfate in 1 ml. of water, and add 0.5 ml. of 3 per cent hydrogen peroxide and 0.5 ml. of 5 N ammonia. Then add 5 ml. of the solution to be tested. In the absence of copper a slight yellow color appears, but with concentrations of copper greater than 1:100,000 a pink color appears at once. With more concentrated solutions a red color forms at once. By means of this reaction 1 part of copper in 300,000 parts of solution can be detected. The color of the reaction mixture at this dilution is a salmon color.

**Detection of antimony.** A yellow amorphous precipitate forms when 1 ml. of a solution of morphine hydrochloride is added to 4 ml. of a cold solution containing 5 g. of antimony trichloride, 20 ml. of concentrated hydrochloric acid and 40 g. of potassium iodide in 100 ml. of water. This reaction may be used for the detection of morphine, or a suitable modification of it may be employed for the detection of antimony.<sup>8</sup>

**Detection of perchlorate.** A 2 per cent aqueous solution of morphine hydrochloride may be used as a sensitive reagent for perchlorates. The perchlorate is identified by means of a crystalline precipitate when the reagent is added to 1 drop of a 0.5 per cent solution of a soluble perchlorate.<sup>9</sup>

**Detection of silica.** Morphine may be identified by its reaction with silicomolybdic acid. A modification of this test may also be used for the detection of silica.<sup>10</sup>

1. F. M. Shemyakin, *Compt. rend. acad. sci. (U.R.S.S.)*, **14**, 115-17 (1937); *C.A.* **31**, 3813 (1937).
2. F. M. Shemyakin, *Compt. rend. acad. sci. (U.R.S.S.)*, **15**, 347-50 (1937); *C.A.* **31**, 8421 (1937).
3. F. M. Shemyakin and V. A. Volkova, *J. Gen. Chem. (U.S.S.R.)*, **7**, 1553-56 (1937); *C.A.* **31**, 8421 (1937).
4. R. D. Hall and E. F. Smith, *Proc. Am. Phil. Soc.* **44**, 196 (1905).
5. R. D. Hall and E. F. Smith, *J. Am. Chem. Soc.* **27**, 1387 (1905).
6. A. Lacroix, *Nouveaux Remedes*, 180 (1902).
7. C. C. Fulton, *Am. J. Pharm.* **105**, 25-9 (1933); *C.A.* **27**, 1843 (1933).
8. M. Caille and E. Viel, *Compt. rend.* **176**, 1156-59 (1923); *C.A.* **17**, 2289 (1923).
9. G. Deniges, *Ann. chim. anal.* **22**, 127-28 (1917); *C.A.* **11**, 2648 (1917).
10. H. Wachsmuth, *J. Pharm. Belg.* **19**, 575-77, 593-95, 609-13, 627-31 (1937); *C.A.* **31**, 8419 (1937).
11. J. Moir, *J. Chem. Met. Mining Soc. S. Africa* **16**, 189 (1916); *C.A.* **10**, 1825 (1916).
12. L. Levy, *Compt. rend.* **103**, 1074, 1195 (1886).
13. L. Levy, *Ann. chim. phys.* [6] **25**, 433 (1892).
14. L. Levy, *Z. anal. Chem.* **40**, 807 (1901).

## NARCEINE

$C_{28}H_{27}O_8N \cdot 3H_2O$

Mol. Wt. 499.27

**Use:** Detection of iodine.

The alkaloid narceine is a white, bitter crystalline solid. The trihydrate melts at 170° C. and the anhydrous compound melts at 145° C. It is very slightly soluble in water but dissolves in alkali hydroxides and dilute mineral acids. It

is slightly soluble in cold alcohol, but is insoluble in benzene, chloroform and ether.

**Detection of iodine.** Narceine yields a blue color with a dilute iodine solution. This reaction has been used for the detection of iodine.<sup>1</sup>

1. P. N. Van Eck, *Pharm. Weekblad.* **62**, 365-76 (1925); *C.A.* **19**, 1828 (1925).

## NARCOTINE

Synonym:  $\alpha$ -Narcotine, opianin, opian, narcosine

$C_{22}H_{23}O_7N$

Mol. Wt. 413.19

Beil. Ref. XXVII, 547, 550.

**Use:** Detection of gold, mercury, nitrate, platinum, and titanium.  
**Determination of nitrate.**

Narcotine is present in opium to the extent of 3-8 per cent. It consists of colorless prisms which melt at 176° C. One g. of the alkaloid dissolves in about 3.3 liters of water, 20 ml. of acetone, 250 ml. of absolute alcohol, 30 ml. of benzene, 2 ml. of chloroform and 250 ml. of ether.

Narcotine is a weak base and does not affect litmus. It may be extracted with organic solvents from strongly acid solutions.

**Detection of gold, platinum and mercury.** Rossi<sup>1,2</sup> has used narcotine in a reagent for the detection of gold, platinum and mercury.

**Reagent.** Mix 5 ml. of a 1 per cent solution of narcotine in concentrated sulfuric acid with 5 ml. of a 10 per cent aqueous solution of stannous chloride and 5 ml. of a 10 per cent aqueous solution of ferrous sulfate.

**Procedure.** Place a drop of the solution to be tested on a strip of filter paper and add a drop of the above reagent. If gold is present, a blue-violet to red-violet color develops. Approximately 0.5% of gold can be detected in this way.

Metals which form insoluble chlorides interfere with this test. Platinum gives a yellow spot. Hexavalent molybdenum is reduced with stannous chloride to yield a blue color, but this disappears on the addition of hydrogen peroxide and ammonium hydroxide. If a drop of the reagent is added to a strip of filter paper, and then a drop of the solution to be tested is placed on this, a yellow color at the edge of the drop indicates the presence of platinum.

Mercury is identified by adding a drop of ammonium hydroxide, which produces a black spot.

**Detection and determination of nitrate.** McRae<sup>3</sup> has used narcotine in a method for determining nitrates in sewage and waters of high chlorine content. This method may be used with fair accuracy for nitrate concentrations ranging from 0.5 to 20 p.p.m. The following method is used in solutions of low nitrate content:

**Reagent.** Dilute a solution of narcotine in concentrated sulfuric acid with water so that the final solution contains 9 parts of acid and 1 part of water, and 1.0 g. of narcotine to 50 ml. of sulfuric acid.



**Procedure.** In a 50-ml. Nessler tube place 5.0 ml. of the solution to be analyzed, or a smaller quantity diluted to 5.0 ml., and add 2.5 ml. of sulfuric acid and cool. Add 10 ml. of the reagent, mix well and read in 20-25 minutes. Compare with standards similarly prepared.

**Detection of titanium.** Titanium may be detected by the brown color which it gives with narcotine.<sup>4,5</sup>

1. L. Rossi, *Quim. e ind.* **12**, 277-8 (1935); *C.A.* **30**, 2131 (1936).
2. L. Rossi, A. Troncoso and M. Giunti, *Rev. farm.* **79**, 369-72 (1937); *C.A.* **32**, 1604 (1938).
3. H. C. McRae, *Am. J. Public Hyg.* **19**, [N.S. 5] 307 (1909); *C.A.* **5**, 2292 (1911).
4. R. D. Hall and E. F. Smith, *Proc. Am. Phil. Soc.* **44**, 196 (1905).
5. R. D. Hall and E. F. Smith, *J. Am. Chem. Soc.* **35**, 138-45 (1913).

## NOVOCAINE

Synonym: Procaine hydrochloride, atoxycocaine, *p*-aminobenzoyl-diethylaminoethanol hydrochloride

$C_{13}H_{20}O_2N_2 \cdot HCl$

Mol. Wt. 272.77

Beil. Ref. XIV, 424.



**Use:** Detection and determination of nitrite.

Novocaine is a colorless, odorless, crystalline solid. It melts at 153-156° C. One g. dissolves in 0.6 ml. of water and 30 ml. of alcohol. It is only slightly soluble in chloroform, and is almost insoluble in ether.

**Detection and determination of nitrite.** Jendrassik and Falcsik-Szabo<sup>1</sup> have substituted novocaine for sulfanilic acid in the reaction with  $\alpha$ -naphthylamine for the detection and determination of nitrites by the Griess reaction. They report more satisfactory results than were obtained by the older method.

**Reagent.** *Novocaine solution:* Dissolve 3 g. of novocaine and 15 ml. of glacial acetic acid in enough water to make 100 ml. of solution.

*$\alpha$ -Naphthylamine solution:* Boil 0.2 g. of  $\alpha$ -naphthylamine with 30 ml. of water for a few minutes, and filter while hot. Wash the filter twice with 30 ml. of water. Add 30 ml. of glacial acetic acid to the filtrate and dilute with water to 150 ml.

**Procedure.** Mix 5 ml. of novocaine solution with 5 ml. of the  $\alpha$ -naphthylamine solution, and then add 5 ml. of the solution to be analyzed. Compare with standards similarly prepared.

By means of the above procedure, and by using a Pulfrich step-photometer, nitrite can be determined at a concentration range of 0.2-35 mg. of nitrite per liter of solution.

1. L. Jendrassik and E. Falcsik-Szabo, *Biochem. Z.* **261**, 110-15 (1933); *C.A.* **27**, 4191 (1933).

**QUINIDINE SULFATE**

(C<sub>20</sub>H<sub>24</sub>O<sub>2</sub>N<sub>2</sub>)<sub>2</sub> · H<sub>2</sub>SO<sub>4</sub>      Mol. Wt. 782.51      Beil. Ref. XXIII, 506(164).

**Use:** Detection of ferricyanide, gold, iridium, osmium, palladium, platinum and rhodium.

The alkaloid quinidine, an isomer of quinine, is present in cinchona bark to the extent of about 0.25-1.5 per cent. It is a white crystalline powder, which slowly darkens on exposure to light. It melts at 170-171° C. when anhydrous. One g. of the alkaloid dissolves in about 2 liters of cold water, 800 ml. of boiling water, 36 ml. of alcohol, 1.6 ml. of chloroform, 56 ml. of ether. It is very soluble in methanol.

Quinidine sulfate, which is commonly used as the analytical reagent, consists of white, bitter crystals. This compound is soluble in 8 parts of water.

**Detection of the platinum metals.** Whitmore and Schneider<sup>1</sup> have investigated the possibilities of quinidine sulfate as a microchemical reagent for the detection of the metals of the platinum group. A solution of the reagent was added to 2 per cent solutions of RuCl<sub>3</sub>, RhCl<sub>3</sub>, PdCl<sub>2</sub>, IrCl<sub>4</sub>, Na<sub>2</sub>OsCl<sub>6</sub>, H<sub>2</sub>PtCl<sub>6</sub> and AuCl<sub>3</sub>. With ruthenium there is no apparent reaction. With rhodium chloride a very slight, yellow, amorphous precipitate gradually forms. A very dense, yellow, granular precipitate forms immediately with the solution of palladium chloride; with iridium a dense, brown, amorphous precipitate forms immediately; with osmium a very fine, dense, yellow, granular precipitate forms immediately; and with platinum a very dense, yellow, granular precipitate forms immediately. When the alkaloid is added to a solution of gold chloride, a dense, yellow, granular precipitate forms immediately; and on standing, and as the drop evaporates, some slender, yellow, needle-shaped crystals appear around the edge of the precipitate, and most of these are arranged in clusters.

**Detection of ferricyanide.** A concentrated solution of quinidine sulfate in acetic acid reacts with ferricyanides to form a crystalline precipitate which is suitable for the microchemical detection of 0.1γ of the ferricyanide ion.<sup>2</sup>

1. W. F. Whitmore and H. Schneider, *Mikrochemie*, **17**, 279-319 (1935).

2. A. Martini, *Anales asoc. quim. Argentina*, **31**, 61-2 (1943); *C.A.* **38**, 529 (1944).

**QUININE**

C<sub>20</sub>H<sub>24</sub>O<sub>2</sub>N<sub>2</sub>      Mol. Wt. 378.25      Beil. Ref. XXIII, 511(166).

**Use:** Detection of antimony, bismuth, cadmium, carbonate, cerium, gold, iridium, osmium, palladium, phosphate, platinum, selenium, sulfate, sulfide, sulfite, tellurium and tin.

Determination of arsenic, bismuth, phosphate and tungsten.

Quinine is the most important alkaloid of cinchona bark. It is a white odorless, very bitter crystalline solid. It darkens on exposure to light. The compound melts when anhydrous at about 175° C. with some decomposition. One g. dis-

solves in 1560 ml. of cold water, 800 ml. of boiling water, 0.8 ml. of alcohol, 80 ml. of benzene, 1.1 ml. of chloroform. The trihydrate is freely soluble in ether, but the solubility decreases with loss of water. The compound is readily soluble in acids. The saturated aqueous solution has a pH of 8.8.

**Detection of bismuth.** Quinine, like many other of the basic nitrogenous compounds, reacts with bismuth salts in the presence of potassium iodide to form an orange-red precipitate. This reaction has been used by various investigators for the detection of small quantities of bismuth.<sup>1-4</sup> Aubry<sup>5,6</sup> has applied this reaction to the detection of bismuth in urine.

**Reagent.** Dissolve 1 g. of quinine sulfate in 20 ml. of water with the aid of 3 or 4 drops of sulfuric acid, and add a solution of 2 g. of potassium iodide in 10 ml. of water. Dilute to 100 ml. with water.

**Procedure.** Evaporate the urine to be tested to dryness and ignite the residue. Dissolve the residue in dilute nitric acid, and add a little of the quinine-potassium iodide solution. An orange-red precipitate forms if bismuth is present. A color is visible at a dilution of 1:600,000  $\text{Bi}_2\text{O}_3$ .

Fabregue and Bressier<sup>7</sup> have used a similar procedure except that glacial acetic acid is used in place of sulfuric acid in the preparation of the reagent. Amodel<sup>8</sup> has further modified Aubry's reagent by dissolving 1 g. of quinine sulfate in 40 ml. of glycerol and adding a solution of 2 g. of potassium iodide in 50 ml. of water.

**Determination of bismuth.** Laporte<sup>9,33</sup> has used the orange-red color which is formed in the reaction between quinine, potassium iodide and bismuth for the colorimetric determination of the latter. The method is based upon the formation of the insoluble orange-red compound, its solution in acetone, and the comparison of the color of the latter with that of standards similarly prepared.

**Reagent.** Dissolve 1 g. quinine sulfate, 3-4 drops of sulfuric acid, and 2 g. of potassium iodide in water and dilute to 100 ml.

**Procedure.** Mix 10 ml. of the bismuth solution in 10 per cent nitric acid (containing 0.1-1.0 mg. of  $\text{Bi}_2\text{O}_3$ ) in a test tube with 2 ml. of the quinine reagent, and add 8 ml. of acetone and compare the color of the resulting solution in a colorimeter with that of a standard similarly prepared.

This method has been reported by Rasmussen and coworkers<sup>32</sup> to give unreliable results.

When Aubry's reagent (quinine and potassium iodide) is added to a solution of a bismuth salt containing bismuth and gum arabic, an orange-yellow, colloidal precipitate is formed, and the intensity of the color varies as the bismuth concentration. This reaction has been made the basis for a colorimetric method for determining small quantities of bismuth.<sup>10</sup>

**Reagent. Bismuth solution:** Dissolve 2.23 g. of  $\text{Bi}_2\text{O}_3$  in sufficient 10 per cent nitric acid to form 1 liter of solution. To 25 ml. of this solution add 175 ml. of 10 per cent nitric acid and dilute to 1 liter.

**Quinine solution:** Dissolve 1 g. of crystalline quinine in 5 ml. of 10 per cent nitric acid and sufficient water to make 100 ml. of solution.

**Procedure.** Mix 5 ml. of the standard bismuth solution with 3 ml. of 10 per cent gum arabic solution, 1 ml. of the quinine solution and 1 ml. of 5 per cent potassium iodide solution. Compare the resulting color with that obtained by mixing 5 ml. of the solution to be examined with the same reagents.

Free acids, except nitric acid, traces of nitrites, iron, copper and several other metallic salts which may oxidize the iodide to free iodine may cause interference with this procedure. Some salts also may cause a flocculation of the colloid.

Okac<sup>11</sup> has proposed the following method for the colorimetric and spectrophotometric determination of traces of bismuth.

**Reagents.** *Quinine reagent:* Dissolve 1 g. of quinine sulfate and 4 g. of sulfuric acid in 50 ml. of water.

*Formate-iodide mixture:* Dissolve 100 g. of sodium formate, 15 g. of potassium iodide, 2 g. of sodium sulfite and 2.5 g. of formic acid in 500 ml. of water.

**Procedure.** Evaporate the sample containing bismuth to dryness with nitric acid and dissolve the residue in 3 ml. of 10 per cent nitric acid solution. Place the solution in a colorimetric cup, heat to boiling, cool, and add 5 ml. of the formate-iodide mixture, and then 1 drop of the quinine reagent. Shake the resulting mixture with 1 ml. of cyclohexanone and compare the red color in the cyclohexanone layer with a color scale prepared in a similar manner with known quantities of bismuth nitrate. From 1-25 $\gamma$  of bismuth can be determined with a colorimetric procedure, while the spectrophotometric method is useful with quantities greater than 25 $\gamma$ .

The red solution of quinine iodobismuthate in cyclohexanone is stable for 3 days in the presence of air and light.

Copper salts interfere, since the latter impart a yellow color to the cyclohexanone solution, and thereby diminish the intensity of the red color due to bismuth. Both thallium and lead interfere with the detection of bismuth. On the other hand silver, mercury, cadmium, arsenic, cobalt, chromium, iron, antimony, aluminum, zinc, magnesium and calcium are without effect upon the above method.

**Detection of antimony and tin.** A solution of quinine and potassium iodide reacts with acid solutions of tin and antimony to yield yellow compounds, which may be used for the detection of these metals.<sup>12,13</sup> Apparently, however, this reaction offers no special advantages over others which have been proposed.

**Detection of cadmium.** Martini<sup>14,35-37</sup> has used quinine sulfate for the microchemical detection of small quantities of cadmium.

**Procedure.** To a small drop of 1 per cent cadmium chloride solution on a glass slide, add a little saturated sodium bromide solution, and a small drop of a concentrated solution of quinine sulfate in concentrated acetic acid. A

white precipitate which shows characteristic crystals under a microscope reveals the presence of cadmium. The crystals may be observed with a solution containing 1 part of cadmium chloride in 2000 parts of solution.

Korenman<sup>38,39</sup> has used the free base in conjunction with potassium iodide for the detection of cadmium. The sensitivity of this reaction is 1:600,000. Lead, mercuric mercury, bismuth, copper, and antimony react similarly.

**Detection of copper.** Cupric salts react with quinine hydrochloride in the presence of potassium iodide to yield a yellow color or precipitate. This reaction is capable of detecting copper at a dilution of 1:900,000. Lead and cadmium react similarly.<sup>38,39</sup>

**Detection of the platinum metals, gold, selenium and tellurium.** Whitmore and Schneider<sup>15</sup> have studied the use of quinine sulfate as a microchemical reagent for the detection of the platinum metals. Their results are shown in Table 44, which is taken from their work.

TABLE 44.—REACTIONS OF PLATINUM METALS WITH QUININE

Test Material	Description
RuCl <sub>3</sub>	No apparent reaction
RhCl <sub>3</sub>	No apparent reaction
PdCl <sub>2</sub>	A very dense, yellow amorphous precipitate forms immediately
Na <sub>2</sub> OsCl <sub>6</sub>	A scant, yellow precipitate forms immediately. This precipitate is composed of a great many small, yellow, rounded granules
IrCl <sub>3</sub>	A reddish-brown, amorphous precipitate forms immediately
H <sub>2</sub> PtCl <sub>6</sub>	A light-yellow, granular precipitate forms immediately
AuCl <sub>3</sub>	A dense, pale-yellow, granular precipitate forms immediately

Goto<sup>16,17</sup> has used quinine for the detection of platinum, gold, selenium and tellurium by means of a fluorescence analysis. As little as 5γ of platinum can be detected with quinine and potassium iodide. The formation of a brown precipitate with this reagent is more sensitive than the disappearance of the quinine-potassium iodide fluorescence. Gold, like platinum, yields a precipitate with quinine and potassium iodide, and there is also a disappearance of the fluorescence of the reagent solution. Selenium and tellurium react like gold and platinum.

**Detection and determination of phosphate.** Phosphates may be determined by a method based upon the yellow coloration which is produced by adding a molybdic acid-quinine reagent to a solution containing a small quantity of phosphate.<sup>18,19</sup>

**Reagents.** *Molybdic acid-quinine reagent:* Dissolve 1 g. of quinine sulfate in dilute nitric acid, and add a sufficient quantity of barium hydroxide solution to precipitate all the sulfate. Filter, and add the filtrate to a solution containing 40 g. of ammonium molybdate in 500 ml. of nitric acid ( $d = 1.20$ ). Dilute to 1 liter and mix.

**Standard phosphate solution:** Dissolve 0.5043 g. of pure crystallized disodium hydrogen phosphate,  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ , in water, add 100 ml. of nitric acid, dilute to 1 liter, and mix thoroughly. Dilute 50 ml. of this solution to 1 liter and again mix. One ml. of this solution contains 0.005 mg. of  $\text{P}_2\text{O}_5$ .

**Procedure.** Place a sample containing 0.002-0.025 mg. of  $\text{P}_2\text{O}_5$  in a 50-ml. Nessler tube and dilute to 45 ml. Add 2 ml. of nitric acid ( $d = 1.12$ ), 2 ml. of the molybdic acid-quinine reagent and dilute to 50 ml. Mix gently and compare the resulting color with that of a series of standards prepared similarly and simultaneously.

Small quantities of silica do not interfere with this determination, but iron must previously be removed by means of cupferron.

Quinine combines with the phosphomolybdate ion to form an extremely voluminous precipitate, which can easily be centrifuged and measured. Street<sup>20</sup> has used this principle for a rapid and fairly accurate method for determining small quantities of phosphorus.

**Reagent.** Mix equal parts of the following:

(a) *Ammonium molybdate reagent:* Dissolve 90 g. of pure ammonium molybdate,  $(\text{NH}_4)_6\text{MoO}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ , in 100 ml. of 6 N ammonium hydroxide, add 240 g. ammonium nitrate, and dilute to 1 liter.

(b) 6 N nitric acid.

(c) *Quinine nitrate reagent:* Dissolve 20 g. of quinine dihydrochloride in 150 ml. of water, heat to boiling, and add an excess of ammonium carbonate. Filter, wash the precipitate until free of chlorides, and dissolve in 50 ml. of 6 N nitric acid. Dilute to 100 ml. with water.

**Procedure.** Place 2-5 ml. of a solution containing about 0.1-0.3 mg. of phosphorus in a centrifuge tube, and add 2-3 ml. of quinine molybdate reagent. Heat on a steam-bath for 5 minutes, and place the tube in a centrifuge, together with a similar tube containing a standard solution of phosphate which has been treated in the same manner as the unknown. Centrifuge the 2 solutions and measure the volumes of the precipitates formed. In this way phosphate may be estimated with an accuracy of approximately 5 per cent.

The reagent described by Street<sup>20</sup> may also be used for the detection of small quantities of phosphate.

**Reagent.** Same as that described for the quantitative determination.

**Procedure.** To 1 ml. of the solution to be tested, add 2 ml. of the reagent and warm to 80-90° C. Allow the mixture to stand 5-10 minutes. A yellow precipitate forms if phosphate is present. This reaction is sensitive to 0.01% of phosphate per drop.

**Determination of arsenic.** Arsenic is determined by a method based upon a formation of a colloidal suspension when quinine arsenomolybdate reagent is added to a solution containing pentavalent arsenic.<sup>21,22,23</sup>

**Reagents.** *Sodium molybdate solution:* Dissolve 3.5 g. of sodium carbonate in 50 ml. of water, add 9.5 g. of molybdic oxide,  $\text{MoO}_3$ , and heat on a water-bath until solution is complete. Cool and dilute the mixture to 100 ml. and mix thoroughly.

*Nitric acid solution:* Dilute 25 ml. of nitric acid ( $d = 1.34$ ) to 100 ml.

*Standard arsenic solution:* Mix 1.3203 g. of pure arsenic trioxide,  $\text{As}_2\text{O}_3$ , with dilute nitric acid and evaporate on a water-bath almost to dryness. Dilute to 1 liter and mix thoroughly. Then dilute 10 ml. of this solution to 1 liter and again mix. One ml. of the diluted solution contains 0.01 mg. of arsenic.

*Quinine arsenomolybdate reagent:* Dissolve 0.5 g. of neutral quinine hydrochloride in 10 ml. of distilled water, add 5 ml. of the standard arsenic solution and 10 ml. of the nitric acid solution, and then add dropwise 1 ml. of the sodium molybdate solution with constant stirring. Upon adding the sodium molybdate solution a precipitate usually forms, but this redissolves in a few minutes leaving a slightly opalescent mixture. Dilute to 120 ml., mix, and filter through a filter which has been washed with dilute nitric acid and then water.

**Procedure.** In the absence of metals precipitated by hydrogen sulfide, proceed as follows: Acidify strongly a sample containing 0.008-0.035 mg. of arsenic and saturate with hydrogen sulfide. Stopper the flask and allow the mixture to stand for 24 hours. Filter through asbestos, wash well and dissolve the precipitate in hot concentrated nitric acid containing a little bromine water. Collect the filtrate and washings, and evaporate to dryness on a water-bath. Dissolve the residue in 20 ml. of the quinine arsenomolybdate reagent. Simultaneously, prepare a standard by adding 0.5 ml. of the nitric acid solution to 2.5 ml. of the standard arsenic solution, 2 ml. of water and 20 ml. of the quinine arsenomolybdate reagent. Allow the solutions to stand for 15 minutes and compare in a colorimeter. The sample may be compared with a series of standards prepared by using varying quantities of arsenic.

If metals of the hydrogen sulfide group are present proceed as follows: Destroy any organic matter with sulfuric acid and nitric acids, heat to expel most of the sulfuric acid, cool the residue (which should have a volume of less than 1 ml.), and dissolve in water. Transfer the solution to a 50-ml. glass stoppered retort, and add a little potassium chloride, a little potassium bromide and a few crystals of hydrazine sulfate. Arrange the retort so that the neck is inclined slightly upward and connect the latter to a vertical bulbed tube, the end of which has been drawn out to a fine opening and dips into a few ml. of water. Carefully distill the solution until nearly colorless and then cool, and then add 1 ml. of concentrated hydrochloric acid and again distill almost to dryness. Repeat this process 3 or 4 times. Now add to the distillate 20-30 ml. of water, 5 ml. of concentrated nitric acid, 5 ml. of bromine water, and evaporate to dryness on a water-bath. Treat the residue with 20 ml. of the quinine arsenomolybdate solution. Allow to stand 15 minutes and compare with the standard as directed above.

Organic matter interferes in the above method of analysis and must be destroyed with the aid of sulfuric and nitric acids, hydrochloric acid and potassium chlorate, or by igniting with calcium oxide or with magnesium oxide and magnesium nitrate. If the latter method is used for the elimination of organic matter, dissolve the residue in the least possible quantity of hydrochloric acid and water, and carry out the distillation as directed in the above procedure.

If antimony and mercury are present, the arsenic must be distilled at a temperature below 115° C. to prevent these metals being carried over into the distillate. It is important to avoid this, since a loss of arsenic will result in the subsequent evaporation.

Excellent results have been obtained by using this method. With quantities of arsenic varying from 0.0025 to 0.0429 mg., errors reported range from 0.001 to 0.0012 mg.

**Determination of tungsten.** Lefort<sup>24</sup> first suggested the use of quinine for the precipitation of tungstic acid. Various other organic nitrogenous compounds, especially chinconine, have since been used for this purpose. Although chinconine is generally employed for this precipitation, quinine has been used in schemes for the gravimetric determination of tungsten.<sup>25,27</sup> The following method may be used for the determination of tungsten in the presence of vanadium.

**Procedure.** If the solution containing tungsten and vanadium is alkaline, neutralize with hydrochloric acid, add 1 ml. of concentrated hydrochloric acid, and 0.5 g. hydroxylamine hydrochloride. Dilute to 100 ml. Boil until the solution turns blue, add 1 ml. of concentrated hydrochloric acid, and then dilute to 200 ml. Add 10 ml. of a 2 per cent solution of arsenic pentoxide,  $As_2O_5$ . Heat to boiling, add quickly a 2 per cent solution of quinine hydrochloride with stirring, and allow the mixture to stand for 12 hours with occasional stirring. Filter, wash with 200 ml. of water containing 2 ml. of concentrated hydrochloric acid, 2 ml. of 2 per cent arsenic pentoxide solution, and 4 ml. of 4 per cent quinine hydrochloride solution. Dry the precipitate, ignite, and weigh as  $WO_3$ .

The above method is suitable for not more than 0.2 g. of  $WO_3$  and 0.2 g. of  $V_2O_5$ . If more than 0.1 g. of either oxide is present, the precipitation should be repeated if the vanadium is to be determined in the filtrate. In the absence of vanadium, reduction with hydroxylamine hydrochloride is unnecessary.

**Detection of germanium.** Vanossi<sup>42,43</sup> has used quinine tannate in a precipitation reaction for the detection of as little as 0.1 $\gamma$  of germanium. The test is carried out in the presence of other substances by converting to germanium tetrachloride, collecting in chloroform or carbon tetrachloride and precipitating with quinine tannate.

**Reagent.** Dissolve 0.05 g. of quinine hydrochloride at 50-70° C. in 10 ml. of 0.02 N hydrochloric acid containing 0.025 g. of tannin.

Make a preliminary test to determine how much hydrochloric acid and how much sodium chloride can be added without precipitating the reagent (see procedure).



**Procedure.** To 0.05 g. of the sample add 0.2-0.3 ml. of concentrated nitric acid, and then 0.2-0.3 ml. of concentrated sulfuric acid, 0.3-0.4 ml. of 70 per cent perchloric acid, and 0.7-0.8 ml. concentrated hydrochloric acid. Add 0.1 g. of boric acid if fluoride is present. Heat gently and distill  $\text{GeCl}_4$  in a stream of air into 3-4 ml. of chloroform or carbon tetrachloride kept 5-10° C. Treat the chloroform solution with 2 volumes of concentrated hydrochloric acid, and transfer to a dry tube. Remove halogens and oxides of nitrogen by treating the chloroform solution with sodium sulfite. A complete purification is effected by treating the chloroform solution with 0.1 ml. of concentrated hydrochloric acid, 0.3 ml. of water, and about 0.1 g. of thiourea. Shake 1 minute and add more thiourea until the chloroform solution is only slightly pink or colorless.

After an additional treatment with 0.3-0.4 ml. of concentrated hydrochloric acid, neutralize the chloroform solution with 0.5 N sodium hydroxide to phenolphthalein, and then add 1.5 N sodium chloride to equal the quantity determined in the preliminary test, and finally add the required quantity of 1.5 N hydrochloric acid. Remove the chloroform, and add quinine tannate to the aqueous solution, which is placed in a constant temperature bath. An opalescence or precipitate forms if germanium is present. Compare with a blank.

**Detection of cerium.** Neutral solutions of ceric salts give an orange or yellow color when treated with 30 per cent hydrogen peroxide and a little quinine hydrochloride.<sup>40</sup> This reaction has been used by Lukas and Jilek<sup>28,41</sup> for the detection of cerium.

This reaction is capable of detecting 0.35% of cerium at a dilution of 1:430,000. Ferric iron interferes and must be absent. This test is recommended as one of the best for cerium.

**Detection of sulfites and sulfides.** If 0.01 N sulfuric acid is added dropwise to about 15 ml. of a quinine solution in a test tube, and this is illuminated horizontally by transmitted filtered ultra-violet light and viewed vertically, a faint blue fluorescence appears. This reaction may be used for the detection of sulfates. Sulfites and sulfides, may also be detected by this method after oxidation to sulfate.<sup>29,30,34</sup> The fluorescence is so sensitive that it is difficult to find oxidizing agents which do not give high blanks. As little as 0.25 mg. of sulfur dioxide can be detected by a procedure based upon the fluorescence of quinine sulfate. As little as 0.1 mg. of sulfide can be detected by a similar reaction.

**Detection of carbonate.** Kubli<sup>31</sup> has used the following reaction to detect sodium carbonate in sodium bicarbonate.

**Reagent.** Dissolve 0.4 g. of quinine hydrochloride in 100 ml. of water.

**Procedure.** Dissolve 3 g. of the bicarbonate to be tested in 50 ml. of water, cool to 10° C., and add an equal volume of the equally cold reagent. A turbidity appears if 2 per cent of sodium carbonate is present.

A turbidity develops at the upper surface of the solution after standing for 5 minutes due to the decomposition of the carbonate.

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## STRYCHNINE

$C_{21}H_{22}O_2N_2$

Mol. Wt. 334.19

**Use:** Detection of antimony, arsenic, borate, bromine, cerium, chlorate chromium, manganese, mercury, nitrate, nitrite, osmium, perchlorate, phosphorus, platinum metals, rhenium and vanadium.

Determination of arsenic, magnesium, mercury, nitrate, nitrite, phosphorus and vanadium.

Strychnine is a colorless or white crystalline solid. It is a violent poison. It melts at 286-288° C., or at 270-271° C. with slow heating.

One gram of the solid dissolves in 6400 ml. of water, 150 ml. of alcohol, 5 ml. of chloroform, 180 ml. of benzene, about 200 ml. of toluene, and 260 ml. of methyl alcohol. Strychnine forms salts with various acids, such as nitric and sulfuric acids, and these salts are commonly used as analytical reagents.

**Detection of phosphorus.** Strychnine molybdate reacts with phosphate to give a bluish-yellow turbidity, which can be used for the detection and the determination of phosphates. This reaction was observed by Pouget<sup>1,2,3</sup> and Pouget and Chouchak,<sup>4,5</sup> who applied it to the detection of strychnine and to the colorimetric determination of phosphoric acid. The following procedure is used for the detection of phosphoric acid.<sup>3</sup>

**Reagents.** *Molybdate reagent:* Dissolve 95 g. of molybdic anhydride and 30 g. of anhydrous sodium hydroxide in 6 ml. of water with aid of heat. Then add 200 ml. of nitric acid ( $d = 1.33$ ) and dilute to 1 liter.

*Strychnine sulfate reagent:* Dissolve 2 g. of strychnine sulfate in 100 ml. of water.

**Procedure.** When ready to use, mix 1 ml. of the molybdate reagent with 10 ml. of the strychnine sulfate reagent, and add a few ml. of this mixture to the solution to be tested. A bluish-yellow to yellow-brown opalescence forms in solution containing only 1 part of phosphoric acid in 2,000,000 parts of water.

West and Houtman<sup>6</sup> have studied various methods for the detection of orthophosphates by means of drop reactions, and have proposed a modification of Deniges'<sup>7,8</sup> strychnine molybdate test. Deniges used a reagent prepared as follows: Dissolve 0.5 g. of strychnine sulfate in water, add 10 ml. of concentrated nitric acid, and 10 ml. of a nitric acid solution of ammonium molybdate prepared according to method of Sonnenschein and Eggertz,<sup>7,8</sup> and dilute to 100 ml. West and Houtman<sup>6</sup> have suggested the following modification of this reagent: Add 2 g. of molybdic acid to 30 ml. of concentrated nitric acid, dilute to 75 ml., and stir until solution is complete. Then add 0.6 g. of strychnine sulfate, and heat gently until all the strychnine sulfate has dissolved. Finally, dilute to 100 ml. and heat slightly below the boiling point for 3-5 minutes until a yellow solution is obtained. A yellow precipitate is formed when 1 drop of this reagent is mixed with 1 drop of a solution containing phosphate. Gold, beryllium, vanadate, arsenate, tungstate, trivalent vanadium, arsenite, antimony, fluoride, oxalate, thiocyanate, trivalent titanium, zirconium and bivalent tin interfere. Sulfide, thiosulfate, iodide, permanganate, ferrocyanide and iridium interfere by masking the color of the reaction. The limit of identification using this method is  $1.6 \times 10^{-6}$  g. of phosphorus.

West and Houtman<sup>6</sup> have proposed a modification of the Deniges strychnine molybdate procedure, which is recommended as being superior to other tests

for phosphates, particularly with regard to interfering substances. This test is identical to the Deniges reaction except that the precipitate formed with strychnine molybdate is treated with a reducing agent. Benzidine proved to be the most satisfactory reducing substance.

**Reagents.** *Strychnine molybdate reagent:* Add 2 g. of molybdic acid to 20 ml. of concentrated nitric acid and dilute to 75 ml. Stir until solution is complete. Add 0.6 g. of strychnine sulfate and heat gently until all of the strychnine sulfate has dissolved. Dilute to 100 ml. and heat slightly below the boiling point for 3-5 minutes until a yellow solution is obtained.

*Benzidine reagent:* Dissolve 0.05 g. of benzidine hydrochloride in 10 ml. of glacial acetic acid and dilute with water to 100 ml.

**Procedure.** Add a drop of the strychnine molybdate reagent to a drop of the solution to be tested on a black spot plate. If a precipitate forms, add a drop of the benzidine reagent and sufficient saturated sodium acetate solution to neutralize the excess acid. A blue-green color is a positive test for phosphate. It is best to repeat the test on a white spot plate, since the blue-green color may be more readily observed against a white background. Trivalent arsenic and vanadium, fluoride, oxalate, arsenate, sulfide, permanganate and ferrocyanide interfere with this test.

Debourdeaux<sup>9</sup> has modified the Deniges reagent by using strychnine nitrate instead of strychnine sulfate. With this reagent it is possible to detect phosphates in the presence of barium.

**Determination of Phosphorus.** The color formed in the reaction between phosphate and strychnine molybdate may be used for the colorimetric or nephelometric determination of phosphate. The following method has been proposed by Clark<sup>10</sup> and is based upon the procedure of Pouget and Chouchak.

**Reagent.** Dissolve 72 g. of molybdic oxide in 150 ml. of an aqueous solution containing 45 g. of sodium hydroxide. Boil for 30 minutes to expel any ammonia, cool, filter, and add 300 ml. of alcohol. Filter, wash with alcohol, and dry at 100° C. The product is sodium molybdate. Dissolve 30 g. of the sodium molybdate in 150 ml. of water and add 50 ml. of concentrated nitric acid very slowly while stirring. Cool and dilute to 250 ml. To a portion of this solution add 0.1 of its volume of a hot solution prepared by dissolving 2 g. of strychnine in hot water containing a few ml. of 9 N sulfuric acid, diluting to 100 ml., and filtering if necessary.

**Procedure.** To determine 10-60 mg. of phosphorus in pure orthophosphate, place 10 ml. of 6 N nitric acid in a 50-ml. Nessler tube, add 3 ml. of the phosphate solution, about 40 ml. of water and exactly 5 ml. of the reagent. Compare the resulting color with that of standard solutions similarly prepared.

Korenman<sup>11</sup> has studied this reaction and reports that from 4-18% of phosphorus can be determined with an average error of approximately 8 per cent. A 100-200 per cent excess of arsenate and metasilicate causes no interference if

the reaction is carried out in an acid solution. Medinger<sup>12</sup> has used a similar procedure for the detection and the determination of traces of phosphates in water.

**Reagent.** To a filtered solution of 40 g. of ammonium molybdate in 100 ml. of water, add gradually about 80 ml. of 1 per cent strychnine nitrate solution until a permanent precipitate is formed. Mix this solution with an equal volume of nitric acid.

**Procedure.** Add 10 ml. of water to be tested to 20 drops of this reagent. The time required for the precipitate or turbidity to form depends upon the amount of phosphate present, and can be estimated by comparison with standards of known phosphate concentration.

Kober and Egerer<sup>13-17</sup> have studied the reaction between phosphate solutions and the strychnine molybdate reagent of Pouget and Chouchak, and have found that quantitative results cannot always be obtained by its use. Further, the reagent gradually becomes yellow on standing and deteriorates, probably due to the reaction of nitric acid. Kober and Egerer have found that by substituting hydrochloric for nitric acid in the reagent, the solution remains practically colorless for a considerable length of time and is stable and gives consistent results. This reagent can be used for the detection of 1 part of phosphorus in 330,000,000 parts of water, and 0.005 mg. of phosphorus in 10 ml. of solution can be estimated quantitatively with the aid of nephelometer. The following method for determining phosphates in urine is taken from the work of Kober and Egerer.<sup>13</sup>

**Reagents.** *Sodium molybdate:* The usual commercial grades of molybdic acid or sodium molybdate are not satisfactory for the phosphate determination. A satisfactory material may be prepared by the following procedure: Boil 35.5 g. of molybdic acid (C.P. free from ammonia, "100 per cent") for about 1 hour with 50 ml. of 10 N sodium hydroxide solution. Dilute the mixture to 84 ml. with distilled water and shake until practically all of the sodium molybdate has dissolved. Add several grams of pure talcum powder, shake thoroughly, and filter. The filtrate should be clear and should not have more than a slight yellowish tint. Evaporate almost to dryness on a water-bath with occasional stirring. Wash the residue by first grinding with 40 ml. of 95 per cent ethyl alcohol, filter, and wash several times on the filter with 20-ml. portions of alcohol. The residue should be perfectly white. Dry in an oven at 50° C., or allow to stand in a vacuum desiccator.

*Strychnine sulfate reagent:* Place 2 g. of pure strychnine sulfate in a 100-ml. volumetric flask, add 80 ml. of water and heat to about 90° C. When all of the solid has dissolved, allow the solution to cool and dilute to the mark with distilled water.

*Strychnine molybdate reagent:* Dissolve 150 g. of sodium molybdate in 250 ml. of distilled water and add slowly with shaking 100 ml. of 1:1 hydrochloric acid. The precipitate which first forms redissolves in excess acid. Add with shaking 150 ml. of the strychnine sulfate solution and allow to stand overnight before filtering. Do not use ordinary filter paper, since the acid solution extracts from

it a substance which causes a marked cloudiness upon standing. Satisfactory papers are S. & S. No. 575 and S. & S. No. 589. The filtered solution should be perfectly clear and practically colorless.

*Standard phosphate solution:* Dissolve 0.1000 g. of potassium dihydrogen phosphate,  $\text{KH}_2\text{PO}_4$ , in a little water, dilute to 2 liters, and mix thoroughly. Dilute 100 ml. of this solution to 1 liter and again mix thoroughly. One ml. of this solution contains 0.005 mg. of  $\text{KH}_2\text{PO}_4$ , which is equivalent to 0.00114 mg. of phosphorus.

**Procedure.** Digest 10 ml. of the urine to be analyzed with 20 ml. of concentrated sulfuric acid and 10 g. of potassium sulfate until a clear solution is obtained. Carry out this digestion exactly as in a Kjeldahl nitrogen determination. Cool and dissolve in water and dilute to 500 ml. Neutralize a 25-ml. aliquot of this solution with ammonium hydroxide, filter through a dry, acid-washed filter paper and dilute the filtrate to 200 ml.

Add 30 ml. of distilled water, 5 ml. of 0.5 N hydrochloric acid and 5 ml. of the strychnine molybdate reagent to each of two flasks and shake thoroughly. To one flask add 10 ml. of the diluted solution of the sample, and to the other add 10 ml. of the standard phosphate solution. The solutions are added slowly with the aid of a pipet while the flasks are gently rotated to insure thorough mixing. Allow the mixtures to stand for 3 minutes and read in a nephelometer. The amount of phosphate in the original sample may be obtained from the nephelometer reading, and from a curve prepared using known quantities of phosphate.

The following procedure is used for the estimation of phosphorus in iron:<sup>14</sup>

**Procedure.** Dissolve 2.00 g. of cast iron borings in 100 ml. of 1:2 nitric acid by boiling. Cool in running water, and dilute the mixture to 100 ml. Withdraw a 5-ml. aliquot, mix with 5 ml. of concentrated sulfuric acid, boil for 2 minutes to eliminate nitric acid, dilute to 100 ml., and filter through a dry acid-washed filter paper. Dilute a 25-ml. aliquot of this solution to 100 ml. Place in each of 2 flasks, 35 ml. of 0.5 N hydrochloric acid and 5 ml. of the strychnine molybdate reagent and shake thoroughly. Add 10 ml. of the diluted sample solution to one flask, and to the other add 10 ml. of standard phosphate solution. Add the solution slowly with the aid of a pipet while gently rotating the flask. Allow to stand for 3 minutes and match the suspensions in a nephelometer.

Clark<sup>10</sup> has studied the strychnine molybdate reagents of Pouget and Kober and Egerer and states that the claim of the latter, that the reagent is colorless and stable, is not completely justified. Further, according to Clark,<sup>10</sup> the reagent of Kober and Egerer cannot be used for the determination of phosphorus in steel, since the large weight of the sample introduces such a large quantity of iron that a yellow color is formed. Belladen and Scazzola,<sup>18</sup> however, have used the method of Kober and Egerer for the determination of phosphorus in steel. Koch,<sup>19</sup> Klinger, Koch and Balschczyk,<sup>20</sup> Hartmann<sup>21</sup> and Miloslavskii and Vavilova<sup>22</sup> have also used a strychnine molybdate reagent for the determination of phosphorus in iron and steel.

Kleinmann<sup>23-27</sup> has proposed a method for the determination of phosphoric acid which depends upon the production of a nephelometric cloud in a sulfuric acid solution of phosphate by means of a strychnine molybdate reagent, and matching the resulting turbidity with that of a standard solution similarly treated. The turbidity is proportional to the phosphoric acid content. In order to obtain accurate results the directions must be closely followed. The following method is taken from the work of Kleinmann.<sup>28</sup>

**Reagents.** The strychnine molybdate reagent is prepared as two solutions, which are mixed just before using. This procedure is necessary since a sediment forms within 24 hours when the molybdate solution and the strychnine solution are mixed and allowed to stand.

*Sodium molybdate solution:* Place 30 g. of pure molybdic acid in a 500-ml. flask and add 10 g. of anhydrous, freshly ignited, sodium carbonate and 200 ml. of distilled water. Heat the mixture slowly to boiling, and boil gently until the solution is perfectly clear. Filter while still hot, and to the filtrate add 200 ml. of exactly 10 N sulfuric acid. Allow to cool and dilute the mixture to 500 ml. in a graduated flask. A clear light blue solution is obtained. The acidity of this solution is a very important factor in the later determination, and so it is important to determine the pH electrometrically after diluting a portion 1:100 with distilled water. The pH of this solution should be 1.41.

*Strychnine sulfate solution:* Dissolve 1.6 g. of strychnine sulfate in about 100 ml. of distilled water with slight warming. Allow to cool and dilute the clear solution with 500 ml. of distilled water.

*Strychnine molybdate reagent:* Pipet equal volumes of the sodium molybdate solution and strychnine sulfate solution into separate flasks, and then quickly pour the strychnine sulfate solution into the ammonium molybdate solution and shake thoroughly. A bluish-white precipitate forms. After a time filter through quantitative filter paper. The clear, colorless solution keeps for about 24 hours. It is best, however, to prepare just before using. The separate solutions will keep indefinitely.

*Standard phosphate solution:* Weigh 1.9167 g. of the purest primary potassium phosphate and dissolve in a little water and then dilute to 1 liter with distilled water and mix thoroughly. This solution contains 1 mg. of  $P_2O_5$  per ml. This is the stock solution. A standard solution is prepared by diluting 5 ml. of the stock solution to 1000 ml. This solution contains 0.005 mg. of  $P_2O_5$  per ml.

**Procedure.** Prepare the sample to be analyzed by evaporating to dryness on a water-bath in a platinum crucible, and then igniting over a Meker burner until the residue is entirely white. If the ash contains any of the heavy metals, these must be removed.

Treat the residue with a few ml. of 2 N sulfuric acid, and warm the crucible on a water bath for 5-10 minutes. Rinse the solution into a graduated flask, treat the crucible several times by warming with 2 N sulfuric acid, and rinse the solution into the flask. Dilute to the mark with 2 N sulfuric acid.

For the determination use a 2 N acid solution of the ash, or a pure phosphate solution whose sulfuric acid content is exactly 2 N. A volume of this solution containing 10-50 $\gamma$  of  $P_2O_5$ , but not greater than 9.5 ml., is used for the analysis.

If the  $P_2O_5$  content of the unknown solution is not known approximately, dilute a portion of the ash solution to 9.5 ml. with 2 N sulfuric acid, then add 4 ml. of saturated sodium sulfate, and dilute with distilled water to 23 ml. Next prepare several solutions of definite  $P_2O_5$  content from the standard phosphate solution for comparison. For example, take 2, 4, and 8 ml. of the standard solution, which is equivalent to 10, 20, and 40 $\gamma$  of  $P_2O_5$ , respectively, and to each add 9.5 ml. of 2 N sulfuric acid and 4 ml. of saturated sodium sulfate solution, and then dilute to 23 ml. with distilled water. To each of these solutions, and to the unknown, add 2 ml. of the strychnine molybdate reagent. Allow to stand for 30 minutes and compare visually the appearance of the unknown with that of the standards, and in this way estimate the approximate phosphate content of the unknown.

Proceed now with the accurate determination as follows: Measure a volume of the ash solution which contains 10-50 $\gamma$  of  $P_2O_5$  into a 50-ml. flask, and dilute with 2 N sulfuric acid to 9.5 ml. If the acid used is not exactly 2 N, the factor must be accurately known and a corresponding volume of the solution used, since it is not the volume of the acid, but its molecular concentration that is important in the determination. Add 4 ml. of saturated sodium sulfate solution to the mixture, and dilute to 22 ml. with distilled water. Prepare a comparison solution by adding 9.5 ml. of 2 N sulfuric acid to a suitable volume of the standard phosphate solution, and dilute with distilled water to 22 ml. The  $P_2O_5$  content of the comparison solution and the unknown must be approximately the same.

To both the standard and the unknown solutions add exactly 2 ml. of the reagent, shake well, and note the time of addition. The solution begins to cloud gradually, and has developed sufficiently for the determination after 30 minutes. Determine whether the unknown contains more or less than 20 $\gamma$  of  $P_2O_5$ . For this purpose a standard containing 20 $\gamma$  of  $P_2O_5$  should be used. From this point different procedures are used depending upon whether the  $P_2O_5$  content is greater or less than 20 $\gamma$ :

(a) When the concentration of  $P_2O_5$  exceeds 20 $\gamma$  in the volume used, add 1 ml. of water to the test solution and to the standard solution, and then measure nephelometrically. The measurement is made 15-20 minutes after the addition of the water, or 30-45 minutes after the addition of the reagent.

(b) If the quantity of  $P_2O_5$  is less than 20 $\gamma$ , add 1 ml. of 2 N sulfuric acid instead of 1 ml. of water to the unknown and the comparison solution, and allow to stand an additional 15 minutes, and then measure during the period from 45-60 minutes after the addition of the reagent.

Rauterberg<sup>28</sup> has determined phosphoric acid with a strychnine molybdate reagent by measuring with a step photometer the transparency of the turbidity formed in the reaction. The reagent and the method are suitable for determining 2.5-40 $\gamma$  of  $P_2O_5$  in 15-20 ml. of solution. Alten, Weiland and Loofman<sup>29</sup> have studied the nephelometric method of Rauterberg,<sup>28</sup> but claim that the method is not satisfactory with regard to the need of development, consistency,



and freedom from interference by salts. It seems to be best suited for the determination of 0.05-0.07 mg. of  $P_2O_5$  per 100 ml. of solution.

Greenwald<sup>30</sup> applied the strychnine molybdate reaction to the determination of phosphates in blood, and this method was later studied by Bloor<sup>31-34</sup> and others.<sup>35-40</sup>

Tereda<sup>41</sup> has proposed a new method for the determination of phosphates by means of strychnine molybdate. The phosphate is first precipitated with strychnine molybdate, the precipitate is then dissolved in sodium carbonate, and finally heated with phenylhydrazine. A red color is obtained which may be compared with that of standard solutions for the estimation of phosphorus.

**Reagents.** *Strychnine molybdate solution:* Dissolve 3 g. of ammonium molybdate in 20 ml. of hot water. Prepare a second solution by dissolving 0.15 g. of strychnine nitrate in 20 ml. of hot water. Transfer both solutions to a 100-ml. volumetric flask and dilute to the mark with 25 per cent nitric acid. Filter before using and stir in a dark bottle.

*Phenylhydrazine solution.* Dissolve 2 g. of phenylhydrazine hydrochloride and 0.5 g. of oxalic acid in 100 ml. of 30 per cent acetic acid. Filter and store in a dark bottle.

*Ammonium phosphomolybdate solution:* Dissolve 0.265 g. of pure dry ammonium phosphomolybdate in 5 per cent sodium carbonate solution and dilute to 200 ml. The  $P_2O_5$  content of this solution is 3.784 per cent.

*Standard color solutions:* Prepare a series of standards by adding different quantities of the stock ammonium phosphomolybdate solution to 10 ml. of the phenylhydrazine hydrochloride solution. Composition of these standards is shown in Table 45:

TABLE 45.

Standard	ml. of ammonium phosphomolybdate solution	mg. $P_2O_5$
A	6	0.3
B	4	0.2
C	2	0.1
D	1.2	0.06

These standards change in 30 minutes in direct sunlight, but can be used after 5-8 days if stored in a dark bottle.

**Procedure.** Place 4-5 ml. of the solution to be analyzed in a centrifuge tube of about 15-ml. capacity, and mix with 5 ml. of the strychnine molybdate reagent. Shake well, allow to stand 1 hour, and then centrifuge. Wash the precipitate 3 times with 5 ml. of 5 per cent nitric acid with stirring and centrifuging. Finally dissolve with 1-2 ml. of 10 per cent sodium carbonate solution with gentle warming. Add to this solution, in the same centrifuge glass, 10 ml. of phenylhydrazine hydrochloride solution and warm for 30 minutes on

a water-bath to 70-80° C. Transfer quantitatively to a 100-ml. volumetric flask, and dilute with distilled water to 100 ml. Compare superficially with standards containing different quantities of stock phosphate solution, and then compare with standards in a colorimeter.

Kirk<sup>42</sup> and Hoagland<sup>43</sup> have determined phosphorus by a procedure which depends upon precipitating phosphate with strychnine molybdate reagent, followed by burning the precipitate and measuring the volume of carbon dioxide formed during the combustion. An empirical factor of 28.4 times as much carbon as phosphorous makes possible a fairly accurate analysis with as little as 0.01 mg. of phosphorus.

**Determination of arsenic.** Belladen, Scazzola, and Scazzola<sup>18</sup> have recommended the determination of arsenic in arsenical copper by means of the method of Kleinmann and Pangritz,<sup>44</sup> but suggest the use of a strychnine molybdate reagent prepared according to the method of Kober and Egerer<sup>15</sup> instead of the cocaine molybdate reagent (page 238).

**Detection and determination of nitrite and nitrate.** A rose color is obtained when nitrites or sulfuric acid solutions of nitrates are treated with strychnine that has been reduced with zinc. The following test has been proposed by Deniges:<sup>45,46</sup>

**Reagent.** Mix 5 ml. of 1 per cent strychnine sulfate, 5 ml. of hydrochloric acid and 5 g. of amalgamated zinc. Heat to boiling and allow to stand for 5-10 minutes and cool.

**Procedure.** Add 0.5 ml. of the above reagent to 10 ml. of water containing a little nitrite. A rose color immediately develops. Nitrates give a similar color provided an amount of concentrated sulfuric acid is added which is equal to one-half the volume of water used.

Kolthoff<sup>47</sup> has modified Deniges' reagent by replacing the amalgamated zinc with pure zinc. Scales and Harrison's<sup>48</sup> modification of this reagent, using magnesium instead of zinc, gives inconsistent results according to Kolthoff.<sup>47</sup>

The red color formed when nitrates react with reduced strychnine is suitable for the colorimetric determination of nitrates. The following procedure is described by Scales and Harrison:<sup>48</sup>

**Reagents.** *Reduced strychnine reagent:* Mix equal volumes of a 0.5 per cent solution of strychnine sulfate in concentrated hydrochloric acid and a 0.1 per cent solution of mercuric chloride in distilled water. Pour cautiously 25 ml. of this mixture over 1 g. of powdered magnesium in a 300-ml. Erlenmeyer flask. Care must be taken in mixing these reagents, since the reaction becomes rather violent. It is best to prepare 2 or more flasks in this way, and combine the reaction mixtures. Allow to cool, filter, and use the filtrate as the reagent. This reagent should be used within a few hours.

*Standard nitrate solution:* Dissolve 6.0677 g. of pure sodium nitrate in water, dilute to 1 liter, and mix thoroughly. One ml. of this solution contains

1 mg. of nitrogen as nitrate. This solution may be diluted to any desired concentration.

**Procedure.** Place 1 ml. of the reagent in a clean test tube, and add 5 ml. of the solution to be tested and 5 ml. of concentrated sulfuric acid. Prepare standards simultaneously and in a similar manner, and compare the colors as soon as they are fully developed. With very dilute solutions of nitrates as much as 30 minutes may be required for color to develop, but only a few minutes are necessary with more concentrated solutions.

The addition of a small quantity of lead, zinc, or mercuric chloride to the strychnine reagent increases its sensitivity. The 0.05 per cent mercuric chloride used in preparation of above reagent gives a reagent sensitive to 1 part of nitrate in 100,000,000 while in the absence of the mercuric salt the sensitivity is only 1 part in 5,000,000. A 0.5 per cent zinc chloride solution or a 0.001 per cent lead solution may be used instead of the mercuric chloride.

Zinc is regarded as an unsatisfactory reducing agent for strychnine, because it usually contains a small amount of lead as an impurity, and the presence of lead yields a reagent which produces a color even with distilled water. Magnesium is recommended in this procedure because it can be obtained relatively pure, it is a vigorous reducing agent, and when employed as directed above gives a reagent which produces no color with water. On the other hand, great care must be taken in reducing the strychnine sulfate in order to obtain an identical reagent each time. The reduced strychnine reagent has been used by various investigators for the determination of nitrate in sea water,<sup>49-52,79</sup> and Sefton<sup>53</sup> has used a similar procedure for the determination of nitrates in battery acid.

**Detection and determination of vanadium.** Pentavalent vanadium reacts with strychnine in sulfuric acid solutions to give a violet coloration which gradually changes to an orange color. This reaction provides a delicate test for vanadium and titanium, molybdenum, tungsten and aluminum do not interfere. Iron, if present, must first be removed by fusion with sodium carbonate. The following method for the determination of vanadium is recommended by Gregory.<sup>54</sup>

**Reagents.** *Ammonium molybdate reagent:* Mix 100 g. of molybdic oxide with 400 ml. of water, and add 80 ml. of ammonium hydroxide solution. Stir well and filter. Pour the filtrate slowly and with constant stirring into a solution of nitric acid prepared by diluting 400 ml. of concentrated nitric acid with 600 ml. of water. Add 0.05 g. of microcosmic salt, allow to stand for 24 hours, and filter.

*Strychnine reagent:* Dissolve 4 g. of pure strychnine in a liter of concentrated sulfuric acid.

*Standard vanadium solution:* Dissolve 0.1785 g. of pure vanadium pentoxide in a small volume of concentrated sulfuric acid, and dilute to 1 liter with concentrated sulfuric acid. Mix thoroughly. One ml. of this solution contains 0.1 mg. of vanadium.

**Procedure.** Dissolve the sample to be analyzed in 40 ml. of 6 N nitric acid and add 1 ml. of 1 N disodium hydrogen phosphate solution. Cool, and add dropwise concentrated ammonium hydroxide until ferric hydroxide just forms, and then boil until it redissolves. Discontinue heating, and add 30 ml. of the ammonium molybdate solution. Stir thoroughly, filter, and wash the precipitate with 2 per cent nitric acid solution until free from iron, and then wash with water. Transfer the precipitate to a large beaker; add a few crystals of potassium chlorate, and 20 ml. of concentrated sulfuric acid, and then evaporate until dense white fumes of sulfur trioxide are given off and chlorine dioxide is no longer evolved. Cool to room temperature, transfer to a Nessler tube, rinsing the beaker with a little concentrated sulfuric acid, and then add 20 ml. of the strychnine reagent. Allow the solution to stand for 10 minutes and compare the resulting color with that of a standard by the method of dilution.

Prepare the standard by measuring a volume of the standard vanadium solution containing approximately the same amount of vanadium as that estimated in the sample to be analyzed, and treat with potassium chlorate and sulfuric acid as described above. Cool and transfer to a Nessler cylinder of the same size as that containing the sample, and add 20 ml. of strychnine reagent. Allow to stand for 10 minutes and compare the solutions, and the one having the more intense color is diluted with concentrated sulfuric acid until the tints in the two tubes match when viewed against a semi-opaque white glass screen.

Moser and Brandl<sup>55</sup> claim that the strychnine method is less satisfactory than that with hydrogen peroxide in concentrated sulfuric acid, and that the thiocyanate and tannin methods are preferable.

Jilek and Vicovsky<sup>56</sup> have found that when 100 ml. of a dilute solution of sodium vanadate containing 7-124 mg. of  $V_2O_5$  is treated with a slight excess of a 2 per cent aqueous solution of strychnine, a precipitate is obtained which can be ignited to  $V_2O_5$ . The results obtained using this method agree with those employing the more tedious mercurous nitrate method of Rose.<sup>57</sup> This method is not satisfactory in the presence of chromates, but chromates can be separated by the use of quinoline.

**Detection of arsenic.** An olive color is formed when 1 ml. of a vanadyl solution, prepared by reducing a 1 per cent metavanadate solution with sulfur dioxide, is added to 4 ml. of an arsenate solution and warmed gently. With a solution of strychnine in sulfuric acid, this mixture gives a rose color, which is characteristic of the higher oxides of vanadium.<sup>80,81</sup>

**Detection of manganese.** Manganese may be detected by the following test proposed by Augusti:<sup>58</sup>

**Procedure.** Place a drop of a manganous salt solution on a watch glass, add a drop of sodium hydroxide solution, let stand for 1 minute, and then gently evaporate to dryness. Add 1-2 small drops of a 1 per cent solution of strychnine in sulfuric acid (66° Bé.). A blue-violet color, changing to red, indicates the presence of manganese.

Cobalt gives a similar test and must be removed or converted to the complex cobalt cyanide ion with potassium cyanide. Chromate, dichromate, and ferro-

cyanide give similar reactions, but these ions are ordinarily eliminated in the usual qualitative procedure so that the above reaction may be used as a confirmatory test in a systematic scheme. The reaction is sensitive to 0.18 $\gamma$  of manganese. The dilution limit is 1:165,000. This reaction has been studied by Dubskey<sup>59</sup> and by Wenger and Duckert.<sup>60</sup> The latter claims that this reaction, while positive, is of less interest than other manganese reactions which have been recommended.

**Detection of chromate.** A violet coloration is obtained when a 1 per cent solution of strychnine in concentrated sulfuric acid is added to chromate or dichromate. Augusti<sup>61</sup> and Wagenaar<sup>78</sup> have used this reaction for the microchemical detection of chromium.

**Procedure.** Evaporate a drop of the solution to be tested to dryness with gentle heating, and add a drop of a 1 per cent solution of strychnine in concentrated sulfuric acid. A violet coloration is a positive test. In this way 0.98 $\gamma$  of chromate or 0.35 $\gamma$  of dichromate can be detected. The sensitivity is 1:900,000.

Manganese, cobalt, ferrocyanide, and ferricyanide interfere, but this interference can readily be eliminated.

**Detection of cerium.** A sulfuric acid solution of strychnine yields a magnificent blue color which slowly changes to violet and then cherry-red when treated with a cerous salt.<sup>62</sup> This reaction may be used for the detection of small quantities of cerium. The following test is proposed by Plugge:<sup>63</sup>

**Reagent.** Dissolve 1 g. of strychnine sulfate in 1000 g. of concentrated sulfuric acid.

**Procedure.** Make the solution to be tested alkaline with sodium hydroxide and evaporate to dryness, and add a few drops of the strychnine reagent to the residue. A blue to violet color develops if cerous salts are present. The reaction is sensitive to 0.01 mg. of cerium oxide.

**Detection of bromine.** Deniges<sup>64</sup> has used reduced strychnine as a sensitive test for bromine.

**Reagent.** Add 5 ml. of hydrochloric acid and 5 g. of amalgamated zinc to 5 ml. of 1 per cent strychnine sulfate solution. Heat to boiling, cool, and decant off the clear liquid.

**Procedure.** Mix 1 ml. of the above reagent with 5 ml. of a bromine solution. A purple-red color appears which shows a characteristic absorption spectrum. This reaction is sensitive to 1:100,000.

**Detection of chlorates, bromates and perchlorates.** Foges<sup>65</sup> has used the following test for chlorates and bromates.

**Reagent.** Dissolve 0.8 g. of strychnine in 24 ml. of nitric acid ( $d = 1.334$ ).

**Procedure.** Add a few drops of the solution to be tested to 1 ml. of the above reagent, and if chlorates or bromates are present a red color develops immediately or within a comparatively short time.

Iodates and perchlorates do not give this reaction. Chlorine, hypochlorites and hydrochloric acid interfere.

Deniges<sup>66</sup> has used a 1 per cent strychnine sulfate solution as a reagent for perchlorate. Characteristic crystals are observed under a microscope when one drop of reagent is added to a drop of the test solution. The reaction is sensitive to one part of perchlorate in 1000 parts of solution.

**Detection and determination of mercury.** Mercury is precipitated as strychnine iodomercurate,  $\text{HgI}_2 \cdot \text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_2 \cdot \text{HI}$ , when strychnine sulfate is added to a solution containing a mercuric salt and potassium iodide. This reaction has been used by Golse and Jean,<sup>67</sup> for the detection of mercury. A 2.5 per cent solution of strychnine sulfate and a 0.5 per cent aqueous solution of potassium iodide are used as the reagent. With this reaction 10 $\gamma$  of mercury at a dilution of 1:500,000 can be detected. Sinyakova<sup>68,69</sup> has used this reaction for the nephelometric determination of small quantities of mercury. Other alkaloids may be used, but strychnine is more satisfactory than quinine since it is less affected by acids.

**Procedure.** Treat 1 ml. of the sample solution containing about 0.002-0.01 mg. of mercury as mercuric chloride with 0.1 ml. of 2.5 per cent strychnine sulfate solution and 0.5 ml. of 0.5 per cent potassium iodide solution. Dilute to 2 ml. and mix well. Compare the turbidity produced with that obtained in a series of standards similarly and simultaneously treated.

For solutions containing 0.002-0.0002 mg. of mercury per ml., proceed as follows:

**Bougault's reagent.** Dissolve 20 g. of sodium hypophosphite in 20 ml. of distilled water, add 200 ml. of concentrated hydrochloric acid, and filter through cotton to remove crystals of sodium chloride. Allow to stand in a cool place until more crystals separate and again filter. Use the clear solution.<sup>70</sup>

**Procedure.** Treat 25 ml. of the sample solution with 0.1 ml. of a solution containing 1.0 g. of arsenious oxide and 5 ml. of N sodium hydroxide solution per liter, and then precipitate arsenic and mercury with Bougault's reagent. Centrifuge the precipitate, wash, and dissolve with bromine, and then remove the excess bromine with a current of air. Add 1 drop of a solution containing 0.01 g. of phenolphthalein and 1 ml. of sodium hydroxide in 100 ml. of water, 1 drop of N sodium hydroxide and then 0.1 N sulfuric acid until the mixture is slightly acid. Dilute with water to 1 ml. and carry out the determination as directed above, preparing a control in a similar manner.

**Detection of antimony.** Antimony is detected by means of the color reaction which is obtained when strychnine and potassium iodide are added to a solution containing antimony ions. This reaction is similar to that of the Caille and Viel reaction using antipyrine.<sup>71</sup>

**Determination of osmium and detection of platinum metals.** Osmium is precipitated as  $\text{Os}(\text{C}_{21}\text{H}_{22}\text{O}_2\text{N}_2)_3$  when a saturated aqueous solution of strychnine sulfate is added to a solution of  $\text{Na}_2\text{OsCl}_6$ . The canary yellow precipitate contains 17.58 per cent of osmium, and can be dried and weighed.<sup>72</sup> Strychnine forms insoluble compounds with all the platinum metals, but the precipitate with ruthenium is soluble in hot alcohol. The ruthenium compound does not separate readily on cooling, and consequently this behavior may be utilized to separate ruthenium from osmium.

Whitmore and Schneider<sup>73</sup> have studied the use of strychnine hydrochloride as a microchemical reagent for the platinum metals. The results obtained by using a 2.5 per cent solution of strychnine hydrochloride with 2 per cent solutions of salts of the platinum metals is given in Table 46.

TABLE 46.—REACTIONS OF PLATINUM METALS WITH  
STRYCHNINE HYDROCHLORIDE

Test Material	Description
$\text{RuCl}_3$	On standing there develop near the circumference of the drop some irregular clusters of very small prisms
$\text{RhCl}_3$	On standing, a brownish flocculent precipitate appears first, then quite a few very small irregular clusters of very small prisms
$\text{PdCl}_2$	A very dense precipitate forms immediately. On close examination this is found to be composed of moss-like structures of fair size. Collectively they form a sort of dense tufted mass
$\text{Na}_2\text{OsCl}_6$	A dense brownish-yellow, granular precipitate forms immediately. Around the edge of this precipitate many small, bright-yellow rectangular prisms appear. Some of these also occur in small clusters
$\text{IrCl}_3$	A very dense, brown flocculent precipitate appears first, then a great many radiating clusters of prisms appear. These are brown and of a fair size
$\text{H}_2\text{PtCl}_6$	A very dense precipitate forms immediately. Around the edge of this precipitate a great many small rectangular plates develop. These occur singly and in radiating clusters
$\text{AuCl}_3$	A dense, yellow precipitate composed of very fine grains is formed immediately

**Detection of rhenium.** Geilmann and Brunger<sup>74</sup> have used strychnine for the microchemical detection of perrhenates, but according to Wenger and Duckert<sup>75</sup> the reaction is not sufficiently satisfactory to be of much value.

**Determination of magnesium.** Denis<sup>76</sup> has used strychnine for the indirect determination of magnesium. Magnesium is precipitated as magnesium ammonium phosphate, and the phosphate content of the precipitate is then determined by means of the strychnine molybdate reaction described above.

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## THEOBROMINE

Synonym: 3,7-Dimethylxanthine

$C_7H_8O_2N_4$

Mol. Wt. 180.09 Beil. Ref. XXVI, 457 (135)

**Use:** Detection of gold and ruthenium.

Theobromine is obtained from cacao beans in which it is present to the extent of about 1.5-3.0 per cent. It is a white, bitter crystalline powder, which sublimes at 290-295° C. One gram of the solid dissolves in about 2 liters of cold water, 2.22 liters of 95 per cent alcohol and 105 ml. of chloroform. It is soluble in alkali hydroxides and in concentrated acids. It is almost insoluble in benzene, ether and carbon tetrachloride. It forms salts which are decomposed by water, and forms compounds with bases which are much more stable.

Theobromine may be isolated from cocoa powder which has previously been freed from fat with ether or petroleum ether in an extractor. The procedure is the same as that employed in extracting caffeine from tea (page 222).

**Detection of ruthenium and gold.** Whitmore and Schneider<sup>1</sup> have used a saturated solution of theobromine as a microchemical reagent for the detection

of ruthenium and gold. When a saturated solution of this reagent is added to a 2 per cent solution of ruthenium chloride, and the mixture allowed to stand for a short time, many brown granules or rounded pellets are formed near the circumference and throughout the drop. Some of these resemble very poorly formed octahedra. With gold chloride a delicate network of fine, long, slender yellow needle-shaped crystals develop around the edge of the drop. Other metals of the platinum group do not give reactions which can be used for their identification.

1. W. F. Whitmore and H. Schneider, *Mikrochemie*, **17**, 279-319 (1935).

## VERATRINE

Synonym: Cevadine

$C_{32}H_{49}O_9N$

Mol. Wt. 591.39

**Use:** Detection of antimony, rhenium, selenium, and tungsten.

Veratrine is a white crystalline solid melting at 205° C. with decomposition. It is extremely poisonous. It is slightly soluble in water and is soluble in 10-12 parts of alcohol or ether. The name veratrine has also been applied to a mixture of the alkaloids, cevadine, veratridine, cevadilline, sabadine and cevine. This mixture is usually designated as veratrine, N.F.V.

**Detection of antimony.** Veratrine is one of the many basic nitrogenous compounds which react with antimony in the presence of potassium iodide to give a yellow precipitate. This alkaloid has been suggested by Caille and Viel<sup>1</sup> as a substitute for quinoline and other nitrogen compounds in the well-known "Caille-Viel reagent."

**Detection of rhenium.** While investigating the analytical reactions of rhenium compounds, Heyne and Moers<sup>2</sup> observed that a number of organic bases, such as veratrine, form crystalline precipitates when added to a 0.5 per cent potassium perrhenate solution. Wenger and Duckert,<sup>3</sup> however, report that the method is not sufficiently sensitive to be of much value as a reagent for rhenium.

**Detection of tungsten.** Tungsten can be detected by converting to tungstic acid, heating with 4-5 times its weight of potassium bisulfate and a few drops of sulfuric acid, and then adding sufficient concentrated sulfuric acid to prevent solidification on cooling. The resulting solution gives an intense sienna color with veratrine.<sup>4</sup>

**Detection of selenium.** Veratrine reacts with selenium to give a red-violet color.<sup>5</sup>

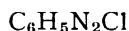
1. Caille and E. Viel, *Compt. rend.* **176**, 1156-59 (1923); *C.A.* **17**, 2289 (1923).
2. G. Heyne and K. Moers, *Z. anorg. allgem. Chem.* **196**, 143-59 (1931).
3. P. Wenger and R. Duckert, *Helv. Chim. Acta*, **25**, 599-604 (1942); *C.A.* **37**, 50 (1943).
4. E. Defacqz, *Compt. rend.* **123**, 308-11 (1896).
5. R. Fritsch, *Z. physiol. Chem.* **104**, 59 (1918); *C.A.* **13**, 2047 (1919).

## CHAPTER X

### DIAZONIUM COMPOUNDS

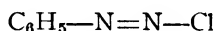
A number of diazotized bases have been used in chemical analysis, and these uses are generally covered in the discussion of the basic compounds. A few, however, are included here.

**DIAZOBENZENE CHLORIDE**      Synonym: Benzenediazonium chloride



Mol. Wt. 140.57

Beil. Ref. XVI, 431



**Use:** Detection of arsenic.

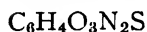
Diazobenzene chloride is an unstable crystalline compound. It explodes on heating. It is very soluble in water, but is only slightly soluble in absolute alcohol and is insoluble in ether. It is soluble in acetone.

**Detection of arsenic.** An intense red color is obtained when an acid solution of an arsenite that has been cooled to  $-5^\circ\text{C}$ . is treated with diazobenzene chloride. This color is stable for about 10 minutes and then changes to yellow. This reaction may be used for the detection of arsenite.<sup>1,2</sup>

1. A. Gutman, *Z. anal. Chem.* **65**, 246 (1924-25).

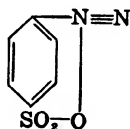
2. G. Gutzeit, *Helv. Chim. Acta.* **12**, 719 (1929).

### DIAZOBENZENESULFONIC ACID



Mol. Wt. 184.17

Beil. Ref. XVI, 561.



**Use:** Determination of aluminum and magnesium.

Diazobenzenesulfonic acid is obtained as colorless needles from water. The compound is soluble in water but is unstable and explodes on heating.

**Preparation:** Dissolve sulfanilic acid in moderately dilute sodium hydroxide, and mix with a little more than the calculated quantity of sodium nitrite. Then add the mixture to an excess of cold dilute sulfuric acid.<sup>1</sup>

**Determination of aluminum and magnesium.** When diazobenzenesulfonic acid is added to the hydroxyquinolates of aluminum and magnesium, it couples with the hydroxyquinoline to form colored solutions which can be used

for the colorimetric determination of magnesium and aluminum. This method has been proposed by Alten and co-workers.<sup>2,3</sup> Magnesium or aluminum is precipitated as the hydroxyquinolate, which is then dissolved in hydrochloric acid and coupled with diazobenzenesulfonic acid. The latter is prepared in solution by the diazotization of sulfanilic acid with nitrous acid. For details of these procedures, see section on 8-hydroxyquinoline.

1. E. Fischer, *Ann.* **190**, 76 Anm. 2.
2. F. Alten, H. Weiland and B. Kurmies, *Angew. Chem.* **46**, 697-8 (1933).
3. F. Alten, H. Weiland and H. Loofmann, *Angew. Chem.* **46**, 668-9 (1933).

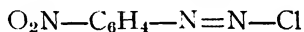
### *p*-NITRODIAZOBENZENE CHLORIDE

Synonym: *p*-Nitrobenzenediazonium chloride



Mol. Wt. 185.55

Beil. Ref. XVI, 483.



**Use:** Detection of ammonium salts.

The free base is not used in analytical procedures, but only as the chloride. The salt is not isolated, but is prepared and used in solution.

**Preparation.** *Riegler's solution:* Add 1 g. of *p*-nitroaniline to 20 ml. of distilled water and 2 ml. of hydrochloric acid and warm until dissolved. Dilute with 160 ml. of water with vigorous shaking, cool, and mix with 20 ml. of a 2.5 per cent sodium nitrite solution. Again shake until solution is complete. The reagent becomes cloudy on standing, but it may be used again after filtering.<sup>1,2</sup>

**Detection of ammonium salts.** A sensitive test for ammonium compounds depends upon the red coloration which forms when *p*-nitrodiazobenzene is treated with a sodium hydroxide solution in the presence of an ammonium salt.<sup>2-7</sup> This reaction appears due to the formation of a colored ammonium salt of *p*-nitrophenylnitrosamine,<sup>8</sup>  $\text{O}_2\text{N}-\text{C}_6\text{H}_4-\text{N}=\text{NONH}_4$ . This reaction cannot be carried out satisfactorily upon filter paper, since the excess of alkali necessary cannot be conveniently added, and a deep red color may be formed even in the absence of ammonium salts. The test may, however, be carried out on a spot plate by means of a procedure proposed by Feigl.<sup>8</sup>

**Procedure.** Place a drop of the slightly acid or neutral solution to be tested in the depression of a spot plate, and add a drop of Riegler's reagent, and then add a small particle of calcium oxide. A red zone forms around the calcium oxide if ammonium salts are present. Color reactions may occur in the absence of ammonium salts, but these are always very slow in developing. For very small quantities of ammonium salts, comparisons should be made with a blank test using a drop of distilled water. With this reaction, 0.67% of ammonia can be detected at a concentration of 1:75,000.

Korenman<sup>6</sup> has used this reagent for the detection of ammonia in air,

1. J. C. Cain and F. Nicoll, *J. Chem. Soc.* **81**, 1432 (1902).
2. E. Riegler, *Chem.-Ztg.* **21**, 307 (1897).
3. F. Feigl, G. Hirsch and I. Tamchyna, *Mikrochemie.* **7**, 10-20 (1929); *C.A.* **23**, 4421 (1929).
4. J. V. Dubsky and M. Novakova, *Chem. Obsor.* **15**, 136-9 (1940); *C.A.* **37**, 49 (1943).
5. G. Gutzeit, *Helv. Chim. Acta.* **12**, 713, 829 (1929).
6. I. M. Korenman, *Z. anal. Chem.* **90**, 115-18 (1932); *C.A.* **27**, 43 (1933).
7. F. Feigl, *Mikrochemie.* **13**, 129-35 (1933).
8. C. R. Fresenius, *Anl. zur qual. chim. Analys.* 17 ed., p. 125 (1919).

## CHAPTER XI

### CARBOHYDRATES

Since the carbohydrates generally contain both hydroxyl and aldehyde or ketone groups, they possess both salt-forming and reducing properties. A number of analytical uses have been based on these reactions. Only a few carbohydrates, however, have been of any particular value in analytical chemistry.

#### CELLULOSE

**Use:** Detection of bismuth, cadmium, cobalt, copper, iodide, iron, lead, mercury, nickel and silver.

Cellulose, after treatment with sodium hydroxide and carbon disulfide, may be used as a reagent for several metals. The reagent is prepared by boiling filter paper with very concentrated sodium hydroxide, cooling, treating with carbon disulfide, and then allowing the mixture to stand overnight. A red, water-soluble, gelatinous liquid, consisting of cellulose and sodium thiocarbonates, is obtained. This solution reacts with solutions of metal salts as follows:<sup>1</sup>

(1) **Lead.** Lead salts in an alkaline solution react with the reagent to form a red precipitate. This precipitate is insoluble in an excess of reagent in neutral or dilute acetic acid solution, and there is a flocculation of viscose impregnated with the red precipitate. On heating the precipitate turns black.

(2) **Nickel.** Nickel salts in an alkaline solution containing a tartrate give a garnet-red color when treated with the reagent in the cold. In an ammoniacal solution, addition of the reagent gives a wine-colored precipitate. This dissolves to form a garnet-red solution with an excess of the reagent.

(3) **Cadmium.** Cadmium acetate, in an ammoniacal solution, reacts with a small quantity of the reagent to give a yellow precipitate which gradually turns to a golden color. The precipitate is insoluble in an excess of reagent.

(4) **Cobalt.** Ammoniacal cobalt nitrate yields with the reagent an apple-green precipitate which dissolves in an excess of the reagent to form a deep-colored solution.

(5) **Mercury.** Mercuric chloride in an ammoniacal or neutral solution reacts with the reagent to form a deep orange precipitate. This gradually turns to a chocolate-brown on standing. With an excess of reagent a black powder is obtained.

(6) **Iron.** Ferrous salts, in the presence of tartrates, yield with one drop of the reagent a wine-colored solution. This turns almost black on adding more reagent, but the color is deep, wine-red. Ferric salts react similarly.

(7) **Silver.** One drop of the reagent added to a solution of silver nitrate yields a dark, gelatinous, flocculent precipitate.

(8) **Copper.** Solutions of copper salts react like those containing silver.

(9) **Bismuth.** Ammoniacal bismuth solutions yield dark precipitates with the reagent.

**Detection of silver.** Whitby<sup>2</sup> has investigated the use of a number of organic reducing agents for the detection and determination of silver, and mentions that cellulose may be employed for this purpose.

**Detection of iodide.** Schumacher<sup>3</sup> has used the following method for the detection of iodides in saliva, urine, and other biological fluids:

**Procedure.** Place a crystal of ammonium persulfate on a piece of filter paper, and add 5-7 drops of the liquid to be tested. If iodide is present, it is oxidized to free iodine, which in turn stains the paper blue.

As little as 0.8γ of iodide can be detected in this way. Some organic iodine compounds give this reaction.

1. G. Loose, *Ingenieur Chimiste*, **9**, 176-8 (1925); *C.A.* **21**, 1943 (1927).
2. G. S. Whitby, *J. Soc. Chem. Ind.* **28**, 749 (1909); *C.A.* **4**, 1444 (1910).
3. I. Schumacher, *Deut. med. Wochenschr.* **41**, 196 (1915); *C.A.* **9**, 1923 (1915).

## DEXTRIN

Synonym: British gum, starch gum and leiocom

**Use:** Detection of silver.

Determination of magnesium and silver.

Dextrin,  $(C_6H_{10}O_5)_n \cdot XH_2O$ , is produced by the partial hydrolysis of starch with dilute acids or by heating dry starch. It is a white or yellow amorphous powder. The white variety is practically odorless, but the yellow form possesses a characteristic odor. The compound is fairly soluble in boiling water, less soluble in cold water, and is insoluble in alcohol and ether.

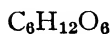
Dextrin is used as a reducing agent for the detection or determination of certain substances, especially silver with which it yields a characteristically colored colloidal suspension.<sup>1</sup>

Perhaps the most important application of dextrin in analytical chemistry is as a protective colloid in the formation of small quantities of lakes which are used in colorimetric comparisons. Typical of this use is the determination of magnesium with titan yellow.<sup>2</sup> The magnesium is precipitated as the hydroxide in the presence of the dye and a little dextrin, whereby a colored lake is formed which can be estimated colorimetrically.

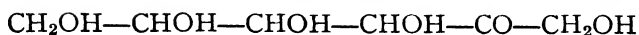
1. G. S. Whitby, *J. Soc. Chem. Ind.* **28**, 749 (1909); *C.A.* **4**, 1444 (1910).
2. E. E. Ludwig and C. R. Johnson, *Ind. Eng. Chem., Anal. Ed.* **14**, 895-7 (1942); *C.A.* **37**, 578 (1943).

**FRUCTOSE**

Synonym: Levulose, fruit sugar



Mol. Wt. 180.16 Beil. Ref. I, 918; XXXI, 321

**Use:** Determination of boric acid.

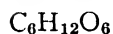
Fructose is a white crystalline powder. It melts at 102-104° C. with decomposition. It is very soluble in water, and freely soluble in alcohol and acetone.

**Determination of boric acid.** v. Liempt<sup>1</sup> has used fructose as a substitute for mannitol in the titration of boric acid, and regards it as somewhat more satisfactory.

1. J. A. M. v. Liempt, *Rec. trav. chim.* **39**, 358-70 (1920); *C.A.* **15**, 216 (1921).
2. S. A. Celsi and M. A. Copello, *Anales farm. bioquim. (Buenos Aires)* **14**, 1-19 (1943); *C.A.* **38**, 38 (1944).

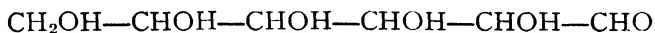
**GLUCOSE**

Synonym: Dextrose, grape sugar



Mol. Wt. 180.16

Beil. Ref. I, 879.



**Use:** Detection of ammonia, bismuth, copper, free oxygen, gold, silver, and tin.

Determination of bismuth and gold.

Glucose consists of white or colorless, odorless, sweet crystals, or is a crystalline powder. It melts at 146° C. It is soluble in water, slightly soluble in alcohol, and insoluble in ether.

**Detection and determination of bismuth.** Solutions of bismuth salts are reduced by glucose in the presence of sodium hydroxide to metallic bismuth. When 4-5 times as much glucose as bismuth salt is present, the reduction is 97.87 per cent complete. Due to the formation of the black, finely divided metal with glucose, this reagent may be used for the detection or determination of bismuth. Bismuth may be determined by weighing the precipitated metal.<sup>1</sup>

**Detection of copper.** Schenk<sup>2</sup> has proposed to use glucose as a sensitive reagent for copper. This reaction is a variety of the well-known Fehling's test for reducing sugars.

**Procedure.** To 10 ml. of the solution to be tested, add a drop of sodium potassium tartarate solution and a trace of glucose, and then immerse the mixture for 2-3 minutes in a boiling water-bath. The presence of copper is indicated by the formation of orange-red cuprous oxide. The test is given with as little as 0.0031 g. of copper per liter.

This reaction is not as delicate as that using potassium ferrocyanide, or tincture of guaiac and hydrogen cyanide,



**Detection and determination of gold.** A violet precipitate is formed by heating to boiling a solution of a gold salt with glucose sugar. This reaction is sensitive to 1 part of gold in 10,000,000 parts of solution, and has been used by Santori<sup>9</sup> for the detection and determination of gold in urine.

A hot, alkaline solution containing 20 per cent glucose causes the rapid reduction of gold salts to metallic gold. No mirror is formed, and the metal settles rapidly in easily filterable form. This reaction may be used for the gravimetric determination of gold.<sup>7</sup>

**Detection of tin.** Stannous chloride reacts with a solution of gold chloride to form a brown or red-brown precipitate. Gutzeit<sup>10,11</sup> recommends as a tin reagent a 1 per cent solution of gold chloride in 0.1 N hydrochloric acid containing 0.5 per cent glucose.

**Detection of silver.** Silver may be detected by reducing its salts to the metal with glucose.<sup>3,8</sup> This test is usually carried out under conditions such that the silver deposits as a mirror. The reduction occurs when a solution of the silver salt is heated with glucose in the presence of sodium hydroxide.

**Detection of ammonia.** Glucose may be substituted for formaldehyde as a reducing agent in a spot test for ammonia, which depends on the formation of a silver mirror.<sup>4</sup>

**Detection of free oxygen.** Glucose, together with methylene blue, may be used for detecting free oxygen.<sup>5</sup>

**Reagent.** Mix 3 ml. of a 10 per cent glucose solution, 1 drop of N sodium hydroxide solution, and 1 drop of a solution of methylene blue prepared by dissolving 30 mg of the dye in 30 ml. of water.

**Procedure.** Dip folded strips of gauze into the above reagent and then introduce into the vessel containing oxygen. The color disappears in one minute at a temperature of 37° C. if oxygen is present.

**Standardization of Fehling's solution.** Main<sup>6</sup> has used glucose for standardizing Fehling's solution.

1. H. Cousin, *J. pharm. chim.* **28**, 179-81 (1923); *C.A.* **17**, 3848 (1923).
2. D. Schenk, *Apoth. Ztg.* **28**, 137 (1913); *C.A.* **7**, 1464 (1913).
3. C. Kollo, *Bul. soc. chim. Romania.* **2**, 95-9 (1921); *C.A.* **15**, 1114 (1921).
4. C. Duval, *Compt. rend.* **211**, 588-90 (1940); *C.A.* **36**, 365 (1942).
5. Rienisdijk, *Nederland. Tijdschr. Geneeskunde.* **1423** (1922).
6. H. Main, *Intern. Sugar J.* **35**, 43 (1933); *C.A.* **27**, 4496 (1933).
7. J. L. Maynard, *Ind. Eng. Chem., Anal. Ed.* **8**, 368-9 (1936); *C.A.* **30**, 7484 (1936).
8. E. Salkowski, *J. prakt. Chem.* **102**, 194 (1921); *C.A.* **15**, 3257 (1921).
9. Q. Santori, *Diagnostica tec. lab. (Napoli) Riv. mens.* **1**, 429 (1930); *C.A.* **26**, 5318 (1932).
10. G. Gutzeit, *Helv. Chim. Acta.* **12**, 713 (1929).
11. G. Gutzeit, *Compt. rend. soc. phys. et hist. nat. Geneve* **45**, 64 (1928).

## GLYCOGEN

Synonym: Animal starch

**Use:** Detection of iodine.

Glycogen is a white, odorless powder. It is soluble in water with a slight opalescence. It is insoluble in alcohol.

**Detection of iodine.** Glycogen reacts with free iodine to form a red-violet color.

## INVERT SUGAR

**Use:** Determination of boric acid.

Invert sugar is a mixture of equal molecular quantities of glucose and fructose.

**Preparation:** Dissolve 7 pounds of granulated sugar in a liter of water and boil until clear. Remove the source of heat and quickly add 25 ml. of 3 N sulfuric acid, stir for 30 seconds, and add 1.5 liters of water to which 25 ml. of 3 N sodium hydroxide solution has previously been added. Stir well and cool.<sup>1</sup>

**Determination of boric acid.** Invert sugar has been used to replace the more expensive glycerol and mannitol in boric acid titrations,<sup>1</sup> although Mellon and Norris<sup>2</sup> report that this reagent is less satisfactory. Three ml. of the above solution of invert sugar is sufficient for titrating 10 ml. of 0.1 N boric acid.

1. G. van B. Gilmour, *Analyst*, **49**, 576-7 (1924); *C.A.* **19**, 1111 (1925).
2. M. V. Mellon and V. N. Morris, *Ind. Eng. Chem.* **16**, 123-6 (1924); *C.A.* **18**, 644 (1924).
3. S. A. Celsi and M. A. Capello, *Anales farm bioquim (Buenos Aires)* **14**, 1-19 (1943); *C.A.* **38**, 38 (1944).

## LACTOSE

Synonym: Milk sugar



Mol. Wt. 360.19

**Use:** Detection of gold.

Lactose consists of white, odorless crystals. It is not nearly so sweet as sucrose. One gram of the sugar dissolves in 4.9 ml. of water, and 2.6 ml. of boiling water. It is very slightly soluble in alcohol and is insoluble in chloroform and ether.

**Detection of gold.** A red-violet color is formed when a solution containing auric chloride is heated to boiling with lactose. Neugebauer<sup>1</sup> has used this reaction for the detection of gold in homeopathic preparations.

1. H. Neugebauer, *Apoth. Ztg.* **44**, 667 (1929); *C.A.* **24**, 4894 (1930).

## STARCH

**Use:** Detection of bromine, cyanide, gold, hydrogen peroxide, hypobromite, iodate, iodide, iodine, magnesium, mercury, nitrite, ozone, palladium, platinum and silver.

**Determination of iodine, magnesium, nitrite, oxygen, and ozone.**

Starch is obtained as granules from wheat, potatoes, rice and corn. It is obtained as a white powder. It is insoluble in cold water or alcohol, but dissolves in hot water to form a jelly on cooling.

**Detection and determination of iodine.** Free iodine reacts with starch in the presence of a soluble iodide or hydroiodic acid to form a blue colored product. Various investigators have suggested that the blue product is a true compound, while others regard it as a solid solution.<sup>1-4</sup> The blue color is probably due to adsorption rather than to the formation of a true compound.<sup>5</sup> Molecular iodine may be adsorbed,<sup>6</sup> but it appears more probable that the color is caused by the adsorption of potassium triiodide<sup>7,8</sup> or of hydroiodic acid.<sup>9,10</sup> According to Mylius<sup>11</sup> and Lonnes,<sup>12</sup> the starch-iodide is the hydroiodic acid compound of an iodine addition product of starch. This compound has been assigned the formula  $[C_{24}H_{40}O_{20}I]_4 \cdot HI$ . The blue product dissociates at low concentration.<sup>13</sup> The color developed increases rapidly with an increase of potassium iodide concentration up to 0.35 N, and then more slowly.<sup>14</sup> Additional information on the character of the blue product may be found in the extensive bibliography on the subject.<sup>15</sup> The use of this reaction as a test for iodine is too well known to require any special discussion.

Korenman<sup>16</sup> has studied the starch-iodine reaction and has found that the sensitivity depends upon a number of factors. These include: (a) Dilution of the solution; (b) height of the liquid; (c) concentration of potassium iodide; (d) concentration of acid; (e) temperature; (f) presence of other salts; (g) nature of illumination; and (h) character of the starch used.

The color produced by treating iodine with starch has been used for the colorimetric determination of the former.<sup>17-19</sup> Fellenberg<sup>20</sup> and Remington and co-workers<sup>21</sup> claim that this method does not yield satisfactory results.

The following method may be used for the determination of iodine:<sup>22</sup>

**Reagents, Starch reagent:** Prepare a paste of 2 g. of soluble starch and 30 ml. of cold water, and add this slowly to 70 ml. of boiling water. Boil for 5 minutes. This solution should be prepared every three or four days.

**Standard iodine solution:** Dissolve 0.25 g. of pure iodine in 0.2 per cent potassium iodide solution and dilute the mixture to 1 liter with 0.2 per cent potassium iodide solution. Each ml. of the solution contains 0.25 mg. of iodine. The iodine solution may be standardized by titrating with sodium thiosulfate.

**Procedure:** Place the sample in a 10-ml. or 25-ml. volumetric flask, and to a second flask add a known quantity of the standard iodine solution. Dilute each to about 40 per cent of the volume of the flask, and to each add a 10 per cent potassium iodide solution to within about 1 ml. of the mark. Mix well and add 1 ml. of starch solution. Dilute to the mark, mix well, and compare the resulting colors.

The blue color formed by the action of iodine on starch has been used in a number of methods for the indirect detection and determination of various substances. These tests are usually based upon the formation of iodine or upon the conversion of iodine into one of its compounds. A few typical examples

of this application of starch as an analytical reagent are given in the following sections.

**Detection of nitrite.** Nitrite may be detected in the presence of nitrate by adding a potassium iodide-starch paste to the very dilute solution to be tested which has previously been acidified with phosphoric acid. A blue color is formed with a trace of nitrite.<sup>23-27</sup> Price<sup>28</sup> claims for this reaction a sensitivity of 1:5,000,000. Trommsdorff<sup>29</sup> used a solution of zinc iodide, starch, and sulfuric acid. Kammerer<sup>30</sup> modified Trommsdorff's test by using acetic acid instead of sulfuric acid.

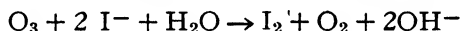
Böttger<sup>31</sup> has used the following reagent for the detection of nitrites:

**Reagent.** Dissolve 1 g. of starch in 200 ml. of water and 1 g. of hydrochloric acid. Add 10 g. of calcium carbonate, and then 10 g. of sodium chloride and 0.5 g. of cadmium iodide. Dilute to 250 ml.

This reagent is colored blue by nitrites.

**Determination of oxygen.** Gaseous oxygen may be determined by its reaction with manganous hydroxide in the presence of potassium iodide.<sup>32</sup> Upon adding starch and acidifying, the blue color of the starch-iodine complex is formed. This may be used for a colorimetric comparison. This method is based on the reaction of Winkler,<sup>33</sup> which was first applied to the colorimetric determination by Rideal and Burgess.<sup>34</sup> Snell<sup>35</sup> has described a procedure with which it is possible to detect 0.15 p.p.m. by volume of oxygen.

**Detection and determination of ozone.** About 0.001 mg. of ozone may be detected by passing the gas through an alkaline or neutral solution of potassium iodide.<sup>36</sup> The reaction is represented by the equation:



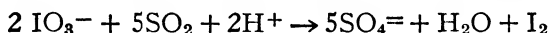
One mole of ozone causes the formation of one mole of iodine. Upon the addition of starch, a blue color is formed which may be used for a colorimetric comparison that indirectly indicates the quantity of ozone originally present. Other oxidizing agents react similarly and must be absent.

**Procedure.** Pass the gas to be analyzed through 20 ml. of a solution containing 0.01 per cent potassium iodide and 0.01 per cent potassium hydroxide until a clear, positive test is obtained on the addition of starch. Note the volume of gas used. Transfer the reaction mixture with thorough washing to a tube graduated at 25 ml., and add 1 ml. of 1 per cent boiled starch paste. Dilute to 25 ml. and compare the resulting color with that of a series of standards similarly prepared and containing 0.001 mg. of iodine and 0.01 mg. of potassium iodide per ml.

The standard iodine solution is prepared as follows: Dissolve 0.1 g. of iodine, 1.0 g. of potassium iodide and 1.0 g. of potassium hydroxide in water and dilute to 1 liter. Dilute 10 ml. of this solution to 1 liter. One ml. of this diluted solution contains 0.001 mg. of iodine. To prepare the standards, dilute different volumes of this solution to 20 ml. with a solution containing 0.01 mg. of potassium iodide and 0.01 mg. of potassium hydroxide per ml.

**Detection of hydrogen peroxide.** A blue color is formed when hydrogen peroxide is added to an acid solution containing potassium iodide and starch paste. This is caused by the oxidation of the iodide to free iodine, which in turn reacts with the starch. By means of this reaction as little as 0.05 mg. of hydrogen peroxide may be detected in a liter of solution.<sup>36</sup>

**Detection and determination of mercury and silver.** Iodates react with sulfur dioxide in an acid solution according to the following equation:



Korenman<sup>37</sup> has found that various substances catalyze this reaction and may be detected by their effect upon the reaction rate. Some ions, such as fluoride, chloride, bromide, iodide, cyanide, thiocyanate, stannous, cupric and manganous, accelerate the reaction, but no satisfactory method of analysis has been based on their activity. Mercury and silver salts, however, retard the above reaction.

The addition of mercury and silver salts to an iodine-starch solution causes a disappearance of the blue color. This reaction may be used to detect mercury and silver salts.

**Procedure.** In one test tube place 2 ml. of water, and in a second tube place 2 ml. of dilute solution to be tested. Add to each several drops of starch and to the test tube containing water, add dropwise a 0.02 per cent aqueous iodine solution to the appearance of a marked blue color. This requires about 5-8 drops of the iodine solution. Now add the same number of drops of the iodine solution to the test tube containing the solution to be tested. In the presence of silver or mercury salts, no color, or only a very weak blue color, is to be observed. By this reaction 0.2γ of mercuric ion can be detected in 5,400,000 parts of solution. Mercurous mercury can be detected at a concentration of 0.14γ per ml., and silver at a concentration of 0.05γ per ml.

Silver may be detected at a dilution of 1:20,000,000. Oxidizing and reducing agents interfere with the above test. West<sup>38</sup> reports that the method of Korenman<sup>37</sup> is one of the most reliable for the detection of mercury.

The action of silver and mercury salts in decolorizing a starch-iodine solution has been used by Korenman<sup>37</sup> for the titrimetric determination of these ions. The solution containing iodide, iodine and starch is added from a buret to the solution of the mercury or silver salt. The point at which all of the mercury or silver has been converted to the iodide is indicated by a failure of the solution to decolorize the starch-iodine mixture.

**Detection of palladium, gold and platinum.** Shapiro (39) states that gold, palladium and platinum salts, like salts of mercury and silver decolorize the blue starch-iodine solution. By this reaction, 0.2γ of gold, palladium or platinum can be detected in 1 ml. of solution.

**Determination of magnesium.** Ludwig and Johnson (40) have used starch as a protective colloid to stabilize the colloidal lake formed in the colorimetric determination of magnesium with titan yellow. Thrun<sup>43</sup> has used starch

for the preparation of starch glycerite for the colorimetric determination of magnesium with turmeric (page 404).

**Reducing action of starch.** When a solution of a silver salt is heated with a little sodium hydroxide solution and starch, a yellow or brown colloidal suspension of silver is formed. This reaction will detect silver at a concentration of 1:25,000,000.<sup>41</sup>

Costeanu<sup>42</sup> has used a similar reaction for the detection and approximate determination of silver. Filter paper is impregnated with an alkaline solution of starch, and the silver is detected by the stain which is formed by applying a solution of the silver salt to the prepared paper. By comparing the stains with those formed using silver solutions of known concentration, the amount of silver present may be estimated.

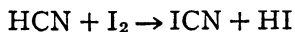
**Detection of bromine.** Free bromine reacts with starch to form an orange color. This reaction can be used to detect bromine, and also bromides, which yield bromine on oxidation. Iodine interferes.

**Detection of iodide.** Basileios<sup>45</sup> has used starch in a procedure for the detection of iodide which is based upon the solvent action of the latter on free iodine.

**Procedure.** Carefully shake 10 ml. of neutralized solution to be tested about 20 times with 2 ml. of a 0.5 per cent solution of iodine in chloroform. Avoid a fine dispersion of chloroform. Add 3 drops of a freshly prepared 1 per cent starch solution, and rotate the container 4 times to mix. The aqueous layer turns blue if iodide is present. This reaction is capable of detecting 6.5γ of iodide at a dilution of 1:750,000. Hypobromite interferes and must be absent. Chlorate, bromate, and iodate do not interfere.

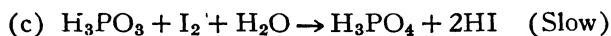
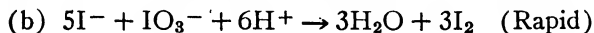
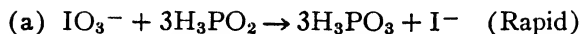
**Detection of hypobromite.** Hypobromite is detected by a procedure similar to that described above for iodide. A blank should be used.<sup>45</sup>

**Detection of cyanide.** Rosenthaler<sup>46</sup> has used starch in a procedure for the detection of cyanides in plant material. The test is based on the reaction



The test is performed by allowing hydrogen cyanide to act on blue iodized starch grains. Decolorization is usually visible to the unaided eye, but a microscope is necessary with small quantities of cyanide. The plant material is first extracted with ether to remove volatile oils and fats, and then covered with water in a flask to form hydrogen cyanide.

**Detection of iodate.** Iodates are reduced by hypophosphorous acid, even in cold solutions, to form iodides; and the free iodine, which is formed in an intermediate reaction, may be detected by the starch reaction. This constitutes an important method for the detection of iodates.<sup>44</sup> Chlorate and bromate do not react under the same conditions. The reactions which occur are represented by the following equations:



The test is performed as follows:

**Procedure:** Place a drop of the neutral solution to be tested on a spot plate, and mix with a drop of starch solution, and then add a drop of a dilute solution of hypophosphorus acid. A transitory blue color is formed if iodate is present.

In this way 1 $\gamma$  of iodic acid can be detected at a concentration of 1:50,000.

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## SUCROSE

Synonym: Cane sugar, saccharose, "sugar"

$C_{12}H_{22}O_{11}$

Mol. Wt. 342.30

**Use:** Detection of boron, cobalt, nitrites and silver.

Determination of calcium, magnesium, silver and vanadium.

Sucrose consists of colorless crystals or white granules or powder. It is characterized by a sweet taste. When heated above 170° C. sucrose chars and gives off the characteristic odor of caramel. One gram of the solid dissolves in 0.5 ml. of water, and 170 ml. of alcohol. It is more soluble in methyl alcohol, but is insoluble in chloroform and ether.

**Separation and determination of calcium and magnesium.** Sucrose reacts like a weak acid to form salt-like compounds with the alkali and alkaline earth hydroxides. Metallic calcium also dissolves in a 30 per cent sucrose solution to form calcium saccharate.<sup>1</sup> The difference in the behavior of calcium and magnesium oxides in the presence of a 30 per cent sucrose solution has been suggested by Shead and Heinrich<sup>2</sup> as a method for the separation and determination of calcium and magnesium. This has been used in the analysis of magnesian limestones and dolomites which are low in silica and iron. When the rock is ignited to a mixture of calcium and magnesium oxides, and the residue extracted with a 30 per cent sucrose solution, calcium oxide dissolves while the magnesium oxide remains behind. After filtration, the residual mag-



nesium oxide may be titrated with a standard solution of an acid. If the mixed oxides are determined by titration of the original limestone, the quantity of calcium present is obtained by difference.

The above method is restricted in its application because if silica is present, calcium silicates, which are insoluble in a 30 per cent sucrose solution, are formed, and these remain behind with the magnesium oxide to give incorrect results. To eliminate this difficulty, Shead and Valla<sup>8</sup> suggested the following procedure: Remove silica and iron and aluminum from the weighed sample of the rock in the usual manner, along with any heavy metals which may be present. From the hot filtrate obtained after these separations, precipitate calcium as the oxalate and magnesium as the 8-hydroxyquinolate. Precipitate these compounds together by dissolving the calculated quantity of 8-hydroxyquinoline in the required quantity of a hot solution of oxalic acid which was saturated when cold. Calcium precipitates first from the slightly acid solution. Then gradually make alkaline with ammonium hydroxide until about 10 per cent by volume has been added, and allow the mixture to stand for 1-2 hours. Filter the mixed precipitate on paper, wash with 2-5 per cent ammonium hydroxide solution and ignite to the oxides in a porcelain crucible containing a piece of platinum foil. Weigh and extract promptly with a 30 per cent sucrose solution. Titrate the magnesium oxide with standard hydrochloric acid according to the usual procedure.

**Detection and determination of silver.** Solutions of silver salts when heated with a little sodium hydroxide and certain organic compounds react to give a yellow or brown color. Such a color is obtained with 50 ml. of a solution containing 1 part of silver in 25,000,000 parts of solution. Among the reagents suggested for this purpose are dextrin, gum arabic, glycerol, cellulose (filter paper), starch and sucrose. Whitby<sup>4-6</sup> recommends sucrose as the most suitable reagent for this reaction, which may be used both for the detection and the colorimetric determination of small quantities of silver.

**Procedure.** To 50 ml. of a silver solution, properly diluted, add a few drops of a fairly concentrated solution of sucrose, and then immerse the beaker containing the solution in boiling water. Heat the mixture for two minutes and add 6 drops of N sodium hydroxide and continue heating for not more than 2 minutes until the color develops. Cool, transfer the solution to a Nessler tube, and compare with standards similarly prepared. The standards should contain 0.000001 g. and 0.000005 g. of silver, and should be prepared not more than 12 hours before using.

Ammonium hydroxide interferes with the above determination, but copper, zinc, mercury, bismuth, cadmium and lead cause no trouble if present in quantities about equal to or lower than that of silver.<sup>7</sup>

**Determination of vanadium.** Salts of tetravalent vanadium liberate equivalent quantities of acid when treated with sucrose. Zolotukhin<sup>8-10</sup> has used this reaction as the basis for a titrimetric method for determining vanadium. The free acid in the tetravalent vanadium salt must be determined separately.

**Detection of cobalt.** Dicyandiamidine sulfate yields no precipitate in ammoniacal solutions of cobalt salts upon the addition of sodium hydroxide. If a sufficient quantity of sucrose is added, a complex ion is formed which prevents the formation of a precipitate of cobalt hydroxide with sodium hydroxide. This complex has a deep red color, and the red color may be observed after the precipitation of nickel with dicyandiamidine sulfate.<sup>11,14</sup>

**Detection of nitrites and the oxides of nitrogen.** Sulfuric acid which contains the oxides of nitrogen yields a green color with  $\alpha$ -naphthol.<sup>12</sup> This reaction may be used to detect 5 parts per million of  $N_2O_3$ , and the sensitivity of this test is increased considerably by superposing upon it the Molisch test, which is obtained by the addition of sucrose. With more than 5 p.p.m. of  $N_2O_3$  a green color is obtained; and with more than 0.06 per cent the upper layer appears yellow. This reaction may also be used to detect as little as 12 p.p.m. of nitrite in an aqueous solution. Ferrous iron, chromate and molybdate interfere, but chloride, bromide, sulfite, thiosulfate, acetate, borate, perchlorate, phosphate, sulfide, barium, strontium, calcium, copper, cadmium, zinc, mercury, lead, manganese and magnesium do not.

**Detection of boron.** Dolgov<sup>13</sup> has suggested the use of sucrose in a test for borate. The solution to be tested and a concentrated solution of sucrose are separately neutralized to a pale pink color with phenolphthalein. If borate is present in the unknown, the color disappears when these two solutions are mixed.

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## CHAPTER XII

### MISCELLANEOUS NATURAL SUBSTANCES

A number of natural products, belonging to no special class of organic compounds, have been found useful in various analytical processes. Due to the diverse character of the materials, they have no common analytical functions. These are included in the following section:

#### AGAR

Synonym: Agar-agar

**Use:** Determination of magnesium, silica, sulfate, tin, and zinc.

Agar is a dried mucilaginous substance extracted from certain species of plants. It is obtained as long, transparent, odorless, tasteless strips, or as a coarse or fine powder. It is insoluble in cold water or in alcohol, but slowly dissolves in hot water to form a viscid solution.

Agar is used principally in analysis as a protective colloid in the colorimetric determination of tin,<sup>1</sup> silica,<sup>2</sup> magnesium,<sup>4</sup> and as a flocculating agent in the quantitative precipitation of zinc sulfide.<sup>3</sup> After precipitating barium sulfate in a hot solution containing 1 ml. of 1 N hydrochloric acid by the slow addition of a 5 per cent barium chloride solution, add dropwise with stirring after each drop 0.5-1 ml. of a 0.1 per cent agar solution. The agar acts as a coagulant by reversing the charge on the particles of barium sulfate.<sup>5</sup>

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#### ALBUMIN

Synonym: Egg albumin

**Use:** Detection of mercury.

Determination of hydrogen, silicon and silver.

Albumin consists of yellow transparent amorphous lumps or scales. It decomposes in moist air with the formation of ammonia. When added to water, it swells at first and then gradually dissolves. The albumin coagulates when the solution is heated at 60-70° C.

**Determination of silver.** Silver may be detected by the dark spot formed when a solution of a silver salt is added to paper that has been impregnated with albumin. By comparing the color of the spot with that produced by

solutions of known silver content, the quantity of silver in the unknown may be approximately determined. By using water repellent materials, and with careful attention to detail, the reaction may be carried out on a surface of limited area and in such manner that the silver deposit is uniformly distributed.<sup>1</sup>

**Determination of silica.** Albumin is used in the determination of silica in Portland cement. It is used to coagulate the precipitate.<sup>2</sup>

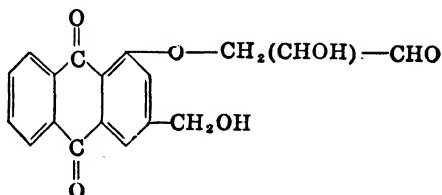
**Determination of hydrogen.** An aqueous solution of sodium anthraquinone-2,7-disulfonate and colloidal palladium, which is peptized by an alkaline solution of sodium protalbinat, may be used for the absorption of hydrogen in gas analysis.<sup>3</sup>

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## ALOIN

**Use:** Detection of copper and cyanide.

Aloin is a mixture of the pentosides obtained from aloe. It varies in chemical composition and physical and chemical properties depending upon the variety of aloe from which it is obtained. One of the compounds is the arabinose glucoside of aloe-emodin, for which the following formula has been suggested:



Aloin is a lemon yellow to dark yellow crystalline powder, which has a slight odor and a bitter taste. It darkens on exposure to air and light. The compound is only slightly soluble in water but is more soluble in alcohol and dissolves readily in acetone. It also dissolves in solutions of alkali hydroxides with a yellow color, which soon turns to red with a green fluorescence. It is also soluble in benzene, chloroform, and ether. Aloin may be substituted for guaiac in the well-known test for copper and cyanide (page 301-302).<sup>1,2</sup>

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## AMBERLITE

Amberlite is an amine-formaldehyde condensation type of resin, known commercially as IR-4. It is a brown solid, sold in a light, flaky, granular form,

and has the appearance of sawdust. It has been used successfully, after saturation with hydrogen sulfide, as a substitute for hydrogen sulfide for the precipitation of insoluble sulfides in the regular schemes of qualitative analysis.<sup>1</sup>

To prepare the precipitant, add just enough water to the resin to form a slurry, and place the mixture in a 1-liter flask. Provide the flask with a 1-hole stopper, fitted with a length of glass tubing; and, after displacing the air in the flask with hydrogen sulfide, stopper tightly, and allow hydrogen sulfide to pass into the flask for several days. The resin adsorbs about 12 per cent of its weight of hydrogen sulfide; and 0.4 g. of the resin, if saturated with hydrogen sulfide, yields about 46 mg. of sulfide ion. The product is very stable if stored in closed bottles or flasks. Decomposition is easily detected by the change in color of the reagent from green to the original brown.

To use, simply add the proper quantity of the reagent (about 0.1 g. per ml. of solution to be tested) and heat on a boiling water-bath for 10 minutes. If the acidity is properly regulated, the sulfides of copper, cadmium, bismuth, lead, mercury, tin, and arsenic are precipitated.

1. S. Gaddis, *J. Chem. Ed.* **19**, 327-8 (1942); *C.A.* **36**, 5107 (1942).

## ARBUTIN

Synonym: Ursin, hydroquinone-glucose

**Use:** Detection of nitrate.

Arbutin is a glucoside having the formula  $C_{12}H_{16}O_7 \cdot \frac{1}{2}H_2O$ . Its molecular weight is 281.13. It consists of white, bitter, silky needles. The anhydrous compound melts at 195-200° C. It is moderately soluble in water and alcohol but is insoluble in chloroform, ether and carbon disulfide.

**Detection of nitrate.** Reichard<sup>1</sup> has used arbutin in the following test for nitrate:

**Procedure.** Mix a drop of the solution to be tested with a drop of a 5 per cent solution of arbutin and evaporate to dryness. Moisten the dry residue with a drop of sulfuric acid. The color changes to a deep permanent yellow if nitrate is present. If free nitric acid is present, the solution should be neutralized with an alkali hydroxide or ammonia before evaporating. Hydrochloric acid may be used instead of sulfuric acid. If the yellow color is absorbed by a strip of filter paper, and a drop of potassium hydroxide solution added, a red-dish-yellow spot appears.

1. C. Reichard, *Chem.-Ztg.* **30**, 790 (1906).

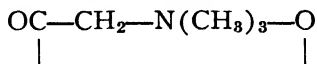
## BETAINE

Synonym: Lycine, oxyneurine, trimethylglycocoll

$C_5H_{11}O_2N$

Mol. Wt. 117.15

Beil. Ref. IV, 333.



**Use:** Detection of gold.

Betaine is widely distributed among various plants, and is usually obtained from sugar beet molasses. It is a colorless deliquescent solid. It possesses a sweet

taste and is neutral in reaction. The compound usually crystallizes with 1 mole of water of hydration, but at 100° C. it becomes anhydrous. The anhydrous compound melts at 293° C. It is soluble in water and in alcohol but is sparingly soluble in ether.

**Detection of gold.** Whitmore and Schneider<sup>1</sup> and Martini<sup>2</sup> have recommended the use of betaine as a sensitive microchemical reagent for gold. When a solid fragment of the compound is added to a solution of auric chloride, a great number of small, bright yellow, square plates, and small cubes form around the test particle immediately. All of the crystals are very well formed. Other metals of the platinum group do not yield precipitates.

1. W. F. Whitmore and H. Schneider, *Mikrochemie*, **17**, 279-319 (1935).
2. A. Martini, *Pub. inst. investigaciones., Univ. nacl. litoral* **3**, 75-93 (1939); *C.A.* **36**, 6105 (1942).

## BORNEOLGLYCURONIC ACID

**Use:** Detection and determination of zinc.

Borneolglycuronic acid is a compound obtained from the urine of a dog which has been fed borneol.

**Preparation:** Mix 5 g. of pulverized borneol with food, and feed to a dog. Collect the urine for a period of 24 hours, acidify, and treat with an excess of lead acetate to remove pigments. Filter and heat the filtrate to boiling and add an excess of zinc acetate. Filter off the precipitate of the zinc salt of borneolglycuronic acid, wash free of coloring matter with hot water and dissolve 100 g. of the zinc salt in 140 ml. of hot 3.5 N sulfuric acid. Cool the mixture rapidly in ice and allow to stand for several hours. Filter off borneolglycuronic acid and wash with cold water. Purify by recrystallizing from hot water.<sup>1,2</sup>

**Detection and determination of zinc.** Zinc is precipitated from an acid or neutral solution with borneolglycuronic acid. The reagent does not form insoluble salts with other common metals except cadmium. Zinc in concentrations as low as 0.03 per cent gives a characteristic crystalline precipitate with a 5 per cent aqueous solution of borneolglycuronic acid. The precipitate corresponds in composition to  $\text{Zn}(\text{C}_{16}\text{H}_{25}\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$ . The precipitate can be weighed directly, or hydrolyzed by boiling with 1.0 N hydrochloric acid for 15 minutes. The glycuronic acid thus formed can be determined by any of the common sugar methods, of which that of Shaffer and Hartmann<sup>3</sup> is the most satisfactory.<sup>2</sup>

Because of the difficulty in preparing the reagent, Wenger and co-workers<sup>4</sup> say that its use is not to be recommended.

1. A. J. Quick, *J. Biol. Chem.* **74**, 331 (1927).
2. A. J. Quick, *Ind. Eng. Chem., Anal. Ed.* **5**, 26 (1933); *C.A.* **27**, 678 (1933).
3. P. Shaffer and A. Hartmann, *J. Biol. Chem.* **45**, 365 (1920-21).
4. P. Wenger, R. Duckert and D. Rieth, *Helv. Chim. Acta*, **25**, 406-15 (1942); *C.A.* **36**, 6438 (1942).

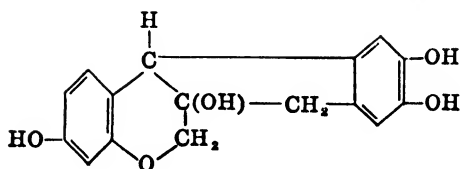
**BRASILIN**

Synonym: Brazilin

 $C_{16}H_{14}O_5 \cdot 1\frac{1}{2}H_2O$ 

Mol. Wt. 286.27

Beil. Ref. XVII, 194

**Use:** Detection of iron.

Brasilin is obtained from Brazil wood or Sappan wood. It consists of amber-yellow crystals which turn orange in air and light. It decomposes when heated above  $130^{\circ}C$ . It dissolves in water, alcohol and ether. It also dissolves in solutions of alkali hydroxides with the formation of a carmine-red color.

**Detection of iron.** Mawas<sup>1</sup> has used a 0.5 per cent aqueous or alcoholic solution of brasilin as a reagent for detecting iron in tissues. The iron forms a dark brown lake, while nuclei are stained violet-red.

1. J. Mawas, *Compt. rend. soc. biol.* **82**, 158-9 (1919).

**CARAMEL****Use:** Determination of oxygen.

Caramel is a dark brown, thick liquid. It has a pleasant, bitter taste, and the odor of burnt sugar. It is soluble in water and dilute alcohol, but it is insoluble in benzene, chloroform, ether, and acetone.

**Preparation:** Caramel is prepared by heating sugar or glucose with the addition of small quantities of sodium carbonate during the heating.

Hamilton<sup>1</sup> has used this compound for the preparation of color standards for the determination of oxygen with pyrogallol. The standard solutions remain unchanged for weeks.

1. E. M. Hamilton, *Eng. Mining J.* **110**, 116 (1920); *C.A.* **14**, 2770 (1920).

**CASEIN****Use:** Determination of silica.

Casein is a protein obtained from milk. It is a white to yellowish granular powder, which is insoluble in water and in organic solvents. It is soluble in dilute mineral acids and in dilute alkali hydroxides. Its principle component is glutamic acid.

**Determination of silica.** In the determination of silica and silicates in portland cement, good results are reported by coagulating the silica precipitate with a 1 per cent solution of casein in sodium hydroxide.<sup>1</sup>

1. P. N. Grigor'ev and P. I. Pozharskaya, *Zavodskaya Lab.* **5**, 1443-44 (1936); *C.A.* **31**, 2965 (1937).

## CELLOPHANE

**Use:** Detection of copper.

Bivalent copper may be detected by means of a colored complex formed with hematoxylin and gelatin or cellophane. For the details of this test, see section on hematoxylin, page 365.<sup>1</sup>

1. C. Duval, *Compt. rend.* **211**, 280-2 (1940); *C.A.* **36**, 55 (1942).

## GELATIN

**Use:** Detection of calcium, copper, phosphate and zinc.

Determination of bismuth, cadmium, calcium, copper, fluorine, silica, silver, sulfate, and zinc.

Gelatin is a product obtained by boiling skin, tendons, ligaments, and bones with water. It is obtained in colorless or slightly yellow transparent, brittle and tasteless sheets, flakes or coarse powder. It swells up and absorbs about 5 or 10 times its weight of cold water, but is soluble in hot water, glycerol and acetic acid. It is insoluble in organic solvents.

**Determination of zinc.** Certain hydrophylic colloids, such as gum arabic and gelatin do not stabilize suspensoid sols if present in minute traces, but instead cause complete and rapid flocculation. This phenomena is called sensitization. Rossi and Scandallari<sup>1</sup> found that very small quantities of gelatin caused the rapid coagulation of sulfur sols. Gelatin has also been used to flocculate sols of antimony trisulfide,<sup>2</sup> and gum arabic has a similar effect upon arsenic sulfide and manganese dioxide sols.<sup>3</sup>

Caldwell and Moyer<sup>4</sup> have used gelatin as a flocculating agent in the quantitative precipitation of zinc sulfide. If 0.5-2.0 mg. of gelatin is added to a zinc solution of appropriate pH, either before or after treatment with hydrogen sulfide, the complete flocculation of 0.3 g. of zinc sulfide takes place immediately. The precipitation is carried out at room temperature, and the mixture may be filtered within 15 minutes. In this way satisfactory separations of zinc are obtained from all other metals of the third analytical group except cobalt. Zinc sulfide obtained in this way can be washed with cold water.

**Procedure.** Dilute a solution containing approximately 0.25 g. of zinc and 6-8 g. of ammonium sulfate and free of chlorides to 250-350 ml. Make just acid to methyl orange and pass hydrogen sulfide rapidly through the mixture for 30 minutes at room temperature. Then add 5-10 ml. of a 0.02 per cent gelatin solution with rapid stirring and allow the precipitate to settle. The gelatin used should contain less than 0.1 per cent ash. The dilute gelatin solution may be preserved for several months by the addition of a few drops of oil of wintergreen. After the mixture has stood for about 15 minutes, filter off the



clear supernatant liquid. Wash the precipitate by decantation with distilled water, which has no peptizing action.

The presence of gelatin causes no interference in the ferrocyanide titrimetric determination of zinc.

If iron is present, wash the precipitate with water containing hydrogen sulfide to keep in a reduced state. The iron is reduced with sulfur dioxide, and the sulfur dioxide is removed with a stream of carbon dioxide before adding hydrogen sulfide.

Results obtained by precipitating zinc in the presence of other metals is given in Table 47. The precipitate was ignited to the oxide before examining for foreign metals.

TABLE 47.—PRECIPITATION OF ZINC IN THE PRESENCE  
OF OTHER METALS

(0.3160 g. ZnO and 0.25<sup>g</sup> g. of other metal present)

Other Metal	Quantity of Other Metal in the Zinc Oxide Precipitate mg.	Ignited Precipitate g.	Deviation g.
Nickel	Less than 0.1	0.3157	—0.0003
Manganese	0.1	0.3164	+0.0004
Manganese	0.1	0.3158	—0.0002
Aluminum	Less than 0.1	0.3163	+0.0003
Aluminum	Less than 0.1	0.3160	±0.0000
Cobalt	5.8	0.3236	+0.0076
Cobalt	7.0	0.3258	+0.0098
Chromium	0.1	0.3162	+0.0002
Chromium	0.1	0.3159	—0.0001
Iron	0.3	0.3166	+0.0006
Iron	0.2	0.3164	+0.0004

**Determination of fluoride.** Fluoride may be determined gravimetrically by precipitation as calcium fluoride. Filtration of the calcium fluoride is facilitated by adding approximately 15 ml. of a 10 per cent gelatin solution to the hot mixture obtained after precipitating the fluoride with calcium chloride.<sup>5</sup>

**Determination of silica.** In the determination of silica in silicates and Portland cement, good results are reported by coagulating the precipitate with a 1 per cent aqueous solution of gelatin.<sup>6</sup>

**Differentiation between zinc and cadmium.** If a drop of a solution of zinc salt and a drop of chromate solution are placed about 1 cm. apart on a layer of gelatin, a striated comb-like arc of yellow zinc chromate is formed. If the zinc solution is placed upon a film of gelatin impregnated with a chromate, Liesgang rings are formed. These phenomena are not observed with cadmium salts. This difference in the behavior of zinc and cadmium has been used by Veil<sup>7</sup> to distinguish between these two metals.

**Determination of copper.** Gelatin has been used to stabilize the copper sulfide hydrosol in the colorimetric determination of small quantities of copper.<sup>8,9</sup>

The colloidal red-brown precipitate formed when potassium ferrocyanide is added to a solution of a copper salt may be used for the colorimetric determination of copper. The precipitate is stabilized with gelatin.<sup>15</sup>

**Determination of cadmium.** Cadmium may be determined colorimetrically by a method based on the formation of a yellow colloidal sol of cadmium sulfide. The colloid is stabilized with gelatin.<sup>16</sup>

**Determination of bismuth.** Bismuth may be determined colorimetrically by forming colloidal bismuth sulfide in dilute acid in the presence of gelatin.<sup>17</sup>

**Detection of copper.** Duval<sup>10</sup> reports that bivalent copper may be detected by means of the colored complex which is formed with hematoxylin and gelatin. For the details of this method, see section on hematoxylin (page 365).

**Determination of silver.** Small quantities of silver may be reduced to a clear yellow sol with sodium hydrosulfite,  $\text{Na}_2\text{S}_2\text{O}_4$ , in the presence of gelatin. The silver may be determined colorimetrically by comparison with standards treated similarly.<sup>11</sup> This method is suitable for determining 1 to 20 p.p.m. of silver.

**Detection and determination of calcium.** Gelatin has been used by Amberg and co-workers<sup>12</sup> in a stabilized ring reaction for calcium. The details of this procedure are given in the section on oleic acid.

Calcium may be determined nephelometrically by precipitating as calcium oxalate. Results accurate to about 20 per cent may be obtained by using gelatin as a stabilizing agent.<sup>14</sup> This method is illustrated by the following procedure:

**Procedure.** Add 10 ml. of saturated ammonium oxalate solution to each of two cylinders. To each add 1 ml. of concentrated ammonium hydroxide and 1 ml. of 0.1 per cent gelatin solution, and mix thoroughly. To one cylinder add the sample, or a suitable aliquot, dilute to 25 ml., and mix well. To the other add a standard calcium solution, and adjust until volume and reflection match.

**Detection of phosphate.** Steigmann<sup>13</sup> claims that the sensitivity of the phosphomolybdate test is enhanced by adding a glycerol-gelatin solution which has been boiled until the protein no longer gives a turbidity with ammonium molybdate. For the details of this test, see section on glycerol.

**Determination of sulfates.** Denis and Reed<sup>14</sup> have determined sulfates and total sulfur in blood by a method based upon the formation of colloidal barium sulfate in uniform suspension with the use of gelatin as a protective colloid. The suspension is then determined nephelometrically. The quantitative precipitation of colloidal barium sulfate as a uniform suspension may be effected only with special attention to detail. The precipitation can be carried out only in the presence of from 0.02 mg. to 0.2 mg. of sulfur in a volume of 25 ml., which contains 1 ml. of 5 per cent gelatin.

1. G. Rossi and G. Scandallari, *Ann. chim. appl.* **23**, 67 (1933).
2. E. Meneghetti, *Bull. soc. ital. biol. sper.* **3**, 779 (1928).
3. A. S. Mennon, *Kolloid-Z.* **38**, 242 (1926).
4. J. R. Caldwell and H. V. Moyer, *J. Am. Chem. Soc.* **57**, 2372-74 (1935); *C.A.* **30**, 987 (1936).
5. N. F. Mikhailova, *Zavodskaya Lab.* **6**, 1154 (1937); *C.A.* **32**, 1209 (1938).
6. P. N. Grigorev and P. I. Pozharskaya, *Zavodskaya Lab.* **5**, 1443-44 (1936); *C.A.* **31**, 2964 (1937).
7. S. Veil, *Bull. soc. chim.* [5] **1**, 1358-59 (1934); *C.A.* **29**, 1744 (1935).
8. L. de Brouckere and S. Solowiejczyk, *Bull. soc. chim. Belg.* **43**, 597-625 (1934); *C.A.* **29**, 1738 (1935).
9. R. H. Muller and A. T. Burtzell, *Mikrochem. ver. Mikrochim. Acta.* **28**, 209-28 (1940); *C.A.* **34**, 7776 (1940).
10. C. Duval, *Compt. rend.* **211**, 280-2 (1940); *C.A.* **36**, 55 (1942).
11. C. F. Miller, *Chemist-Analyst.* **25**, 8-10 (1936); *C.A.* **30**, 1326 (1936).
12. S. Amberg, J. Landsbury and F. Sawyer, *J. Am. Chem. Soc.* **50**, 2630 (1928).
13. A. Steigman, *Chem.-Ztg.* **60**, 129 (1936); *C.A.* **30**, 6672 (1936).
14. E. P. Garmash, *Zavodskaya Lab.* **8**, 13-4 (1933).
15. H. Hahn, R. Juza and R. Langheim, *Z. anal. Chem.* **110**, 270 (1937).
16. R. Juza and R. Langheim, *Angew. Chem.* **50**, 255 (1937).
17. F. Malengreau and G. Delrue, *Arch. intern. med. exptl.* **1**, 35 (1924).

## GINGER PIGMENT

**Use:** Detection of aluminum.

Ginger is the dried rhizome of certain plants found in southern Asia and all tropical countries. It contains 1-3 per cent of a volatile oil, acrid resin, and gingerol.

**Detection of aluminum.** An extract of the yellow ginger pigment in acetic acid which is mixed with an equal volume of sodium acetate gives a blue-violet color when added to a solution containing aluminum. This color is stable toward heat, and can be used for the detection of aluminum.<sup>1</sup>

1. F. Oberhauser, *An. fac. filos. educac., Univ. Chile, Secc. quim.* **2**, No. 2-3, 65-72 (1938); *Chem. Zentr.* **I**, 435 (1940); *C.A.* **35**, 5819 (1941).

## GUAIAIC RESIN

Synonym: Guaiacum, gum guaiac

**Use:** Detection of chromium, copper, cyanide, and iron.

Guaiac resin is obtained from the wood of certain species of trees. It contains about 70 per cent  $\alpha$ - and  $\beta$ -guaiaconic acids, about 10 per cent guaiaretic acid, 15 per cent vanillin, guaiac yellow, and guaiac saponin. The resin occurs as brown, or greenish-brown irregular lumps. It melts at 85-90° C. It is insoluble in water, freely soluble in alcohol, chloroform, ether, and alkalies, and slightly soluble in benzene and carbon disulfide.

Guaiac resin, in the presence of soluble cyanides, reacts with copper salts to give a blue color. This reaction serves as a very sensitive reaction either for copper or cyanides.

**Detection of hydrogen cyanide.** The reaction for cyanides has generally been applied to the detection of gaseous hydrogen cyanide. Solid cyanides, or

cyanides in solution may be detected by first converting to hydrogen cyanide with mineral acids.<sup>1-4,14</sup> This test is carried out as follows:

**Reagent.** Dissolve 0.1 g. of guaiac resin in 50 ml. of 95 per cent alcohol and mix with 15 ml. of a 0.1 per cent solution of copper sulfate. The guaiac resin solution should be prepared fresh every day.

**Procedure.** Place the sample to be tested in an Erlenmeyer flask, and in the mouth of the flask place a strip of filter paper that has been moistened with the guaiac resin-copper sulfate reagent. The paper is held in place by means of a stopper. The paper turns blue with hydrogen cyanide. As little as 0.001 mg. of HCN in 10 ml. of water gives the blue color within three minutes.

If the solution to be tested contains a soluble cyanide, this is converted to hydrogen cyanide with a little mineral acid.

Anderson<sup>8</sup> has studied a number of common methods for detecting hydrogen cyanide in solution and has expressed the sensitiveness of these reactions in Table 48.

TABLE 48.—SENSITIVENESS OF HYDROGEN CYANIDE TESTS

In the second column is given the number of mg. of HCN in 10 ml. of solution that can be detected at the dilution given in column three.

Precipitation as AgCN	0.004 mg.	1:245,000
Prussian blue test	0.040 mg.	1:24,500
Formation of Fe(SCN) <sub>3</sub>	0.004 mg.	1:245,000
Picric acid (alkaline solution)	0.400 mg.	1:2,450
Guaiac tincture—CuSO <sub>4</sub>	0.0004 mg.	1:2,450,000

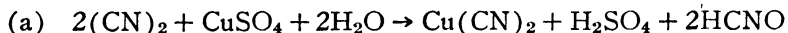
Kolthoff,<sup>4</sup> in a more recent investigation, offers the following comments on a number of the more important hydrogen cyanide tests:

- (a) The Prussian blue and thiocyanate reactions are specific.
- (b) Several substances give the picric acid reaction.
- (c) The guaiac resin test is the most sensitive, but has little or no value, since various oxidizing agents give the same reaction in the absence of hydrogen cyanide, and various reducing agents mask the true hydrogen cyanide reaction.
- (d) The phenolphthalein test is better, since the principal disturbing factor is hydrogen sulfide.
- (e) Precipitation as silver cyanide is reliable after taking precautions to prevent precipitation of the silver halides.
- (f) All of the above reactions can be made quantitative except that with gum guaiac.

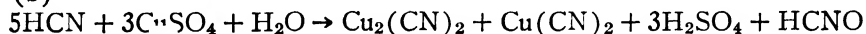
A number of the above reactions take place in the presence of mustard oil, and in the absence of hydrogen cyanide.

Katz and Longfellow<sup>5</sup> have proposed a field test for hydrogen cyanide in air, using gum guaiac, and they claim results agreeing within 20 per cent of those obtained by chemical analysis.

Venturoli and Finzi<sup>6</sup> have studied the gum guaiac-copper sulfate-hydrogen cyanide reaction, and ascribe the formation of the blue color to the action of HCNO (formed from HCN) on gum guaiac. The formation of HCNO under the conditions of the test is shown in the following equations:



(b)



**Detection of copper.** Copper can be detected by an application of the gum guaiac reaction for hydrogen cyanide.<sup>15-18</sup> Paper impregnated with guaiac tincture and dilute potassium cyanide solution is colored blue by a very dilute solution of a copper salt. A very dilute solution of potassium cyanide with guaiac tincture reacts similarly.<sup>7</sup> The following procedure is used:<sup>8</sup>

**Procedure.** Place 5-10 ml. of a dilute solution to be tested in a test tube, add 3-4 drops of a freshly prepared tincture of guaiac, and then slowly add a few drops of potassium cyanide solution. If the solution to be tested is neutral, use a 0.15 per cent potassium cyanide solution, or if the unknown is acid, use a 1.5 per cent potassium cyanide solution. This test is given with 1 mg. of copper in one liter of solution if 5-10 ml. of solution is used.

The characteristic blue color does not appear in an acid solution until the acid is neutralized with potassium cyanide, but if too much cyanide is used, the test is obscured by the brown color formed with potassium cyanide and the resin.

Purgotti<sup>9</sup> has modified the above test somewhat by adding potassium chloride and guaiac tincture to a copper salt solution to obtain a blue color.

A deep blue precipitate, which is insoluble in the usual organic solvents, is formed by adding to a dilute aqueous copper salt solution 3-4 drops of a dilute solution of ammonium thiocyanate and a few drops of 0.5 per cent alcoholic gum guaiac.<sup>10</sup> This reaction constitutes a rather sensitive test for copper and a less sensitive test for thiocyanate. The reaction is given by one part of copper in 10 million, or by one part of thiocyanate in 130,000 parts of solution.

Poirot<sup>11</sup> uses a somewhat different and more sensitive method for detecting copper in distilled water.

**Reagent.** Dissolve 10 g. of purified gum guaiac in 100 ml. of colorless pyridine.

**Procedure.** To 0.2 ml. of the above reagent add 3 drops of 1:10 hydrogen peroxide solution, 10 ml. of 95 per cent ethyl alcohol, and 10 ml. of the dilute copper solution. A deep blue color is formed with copper. Copper is detected by this test in a dilution of 1:100,000,000.

The blue compound is soluble in ethyl alcohol, chloroform, amyl alcohol, and ethyl acetate. It is slightly soluble in ether, benzene, toluene, and insoluble in xylene, carbon disulfide and petroleum ether. It is decolorized by acids and ammonium hydroxide.

Quartaroli<sup>12</sup> used tincture of guaiac to detect copper in biological media. This method is sensitive to 1 part of copper in 1 million of water.

Rosenthaler<sup>13</sup> also used gum guaiac as a reagent for a microtest for copper.

**Detection of chromium.** A blue color is obtained when a solution of chromate in dilute sulfuric acid is treated with gum guaiac.<sup>19,20</sup> This reaction is sensitive to 1:1,000,000. Iron and copper interfere.

**Detection of iron.** In a neutral or weakly acid solution, ferric salts react with gum guaiac to form a blue color. According to Simon and Kotchau<sup>21</sup> this reaction is more sensitive than that with benzidine, and is capable of detecting 0.0056 mg. of iron per liter of solution. Extraction with chloroform intensifies the test. Copper and chromate react similarly.

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## GUM ARABIC

Synonym: Acacia

**Use:** Detection of silver.

Determination of aluminum, antimony, arsenic, bismuth, magnesium, and selenium.

Gum arabic is the dried gummy exudation from certain trees growing chiefly in Africa. It consists essentially of arabic acid (arabin, gummic acid) combined with calcium, magnesium, and potassium and bassorin, cerasin, dextrose, and

pentosan. It occurs as yellowish-white to light-amber lumps of various sizes, or as angular fragments. It is insoluble in alcohol, but slowly dissolves in two parts of water.

**Analytical uses.** Gum arabic is used in analytical chemistry as a protective colloid to prevent the settling of precipitates in certain colorimetric or nephelometric determinations. The following examples illustrate this usage:

(a) *Determination of aluminum:* Thrun<sup>1</sup> uses gum arabic to keep the aluminum lake of aurin tricarboxylic acid in solution in the colorimetric determination of aluminum.

(b) *Determination of magnesium:* Gum arabic is used for stabilizing the lake formed in the determination of magnesium with quinalizarin.<sup>9</sup>

(c) *Determination of arsenic:* Gum arabic may be used as a protective colloid in the colorimetric determination of arsenious sulfide.<sup>5</sup>

(d) *Determination of bismuth:* Gum arabic may also be used as a stabilizer for quinine iodobismuthite in the determination of bismuth by the method of Aubury (page 252).<sup>6</sup> It has also been used to peptize the red bismuth precipitate with dimercaptothiodiazole or phenyldithiodiazolonethiol for the colorimetric determination of bismuth.<sup>7,12</sup> Bismuth may also be determined colorimetrically by precipitating as the colloidal sulfide in a basic solution in the presence of gum arabic.<sup>10</sup>

(e) *Determination of antimony:* Gum arabic may be used as a protective colloid in the precipitation of colloidal antimony sulfide for the colorimetric determination of antimony.<sup>8</sup>

(f) *Determination of selenium:* Gum arabic is used in a colorimetric method to stabilize the selenium sol formed by the reduction of selenium compounds with phenylhydrazine or sodium bisulfite.<sup>11</sup>

**Determination of silver.** Costeanu<sup>2</sup> and Whitby<sup>3,4</sup> have used a number of reducing agents, including gum arabic, for the reduction of silver nitrate to metallic silver. Silver may be detected by treating paper impregnated with an alkaline solution of gum arabic with the solution to be tested. This method may be made semi-quantitative.

1. W. E. Thrun, *Ind. Eng. Chem., Anal. Ed.* **2**, 8-9 (1930); *C.A.* **24**, 1052 (1930).
2. N. D. Costeanu, *Mikrochemie*, **26**, 170-4 (1939); *C.A.* **33**, 3290 (1939).
3. G. S. Whitby, *Z. anorg. Chem.* **67**, 62 (1910); *C.A.* **4**, 1444 (1911).
4. G. S. Whitby, *J. Chem. Soc.* **98**, II, 654 (1910).
5. V. Mertens, *J. pharm. Belg.* **23**, 497-502, 529-32 (1941); *C.A.* **37**, 3007 (1943).
6. L. Cuny and G. Poirot, *J. pharm. chim.* **28**, 215 (1923).
7. A. K. Majunbar, *J. Indian Chem. Soc.* **19**, 396 (1942); *C.A.* **37**, 4320 (1943).
8. P. Schidrowitz and H. A. Goldsborough, *Analyst*, **36**, 101-3 (1911).
9. A. Thiel and E. van Hengel, *Ber.* **71B**, 1157 (1938).
10. L. Malossi, *Rend. accad. sci. Napoli*, **2**, 83 (1932).
11. R. Dolique, J. Giroux and S. Roca, *Bull. soc. chim.* **10**, 49-50 (1943); *C.A.* **38**, 5469 (1944).
12. A. K. Majundar, *J. Indian Chem. Soc.* **21**, 240-4 (1944); *C.A.* **39**, 2263 (1945).

**HYMOLAL**

Synonym: Drene, dreft, gardinol

**Use:** Detection of potassium.

These commercial detergents consist of the sulfates of lauryl or higher alcohols. The general formula,  $\text{CH}_3-(\text{CH}_2)_n-\text{O}-\text{SO}_3\text{Na}$ , where  $n$  is 10 or greater, may be used to represent these substances. These materials were first suggested by Wildman<sup>1</sup> as a reagent for the detection of potassium:

**Procedure.** Divide the filtrate containing the alkali metals, obtained in the usual scheme of analysis, into 3 parts. Use 2 portions for the detection of magnesium and sodium. From the third, remove ammonium salts as usual and dissolve the residue in about 15 ml. of water which contains a few drops of acetic acid. Filter if not clear and to 5 ml. of the filtrate add 1 ml. of a 3 per cent solution of the reagent. A white precipitate forms within 1 minute if potassium is present.

Reichert<sup>2</sup> claims that this test is less delicate than that with sodium cobaltinitrite, but states that for the detection of larger quantities of potassium, gardinol W may readily be substituted because of its cheapness.

Drene has been studied as a possible microchemical reagent for potassium by Frediani and Gamble.<sup>3</sup> An amorphous precipitate is obtained with 8γ of potassium. Salts of lithium, ammonium, magnesium, sodium, and calcium are reported as soluble in water. Negative tests are obtained with ammonium, antimony, arsenic, mercury, cadmium, copper, cesium, lithium, manganese, rubidium, silver and sodium.

1. E. A. Wildman, *Proc. Ind. Acad. Sci.* **44**, 121-3 (1934); *C.A.* **30**, 407 (1936).
2. B. Reichert, *Arch. Pharm.* **273**, 232-3 (1935); *C.A.* **29**, 3939 (1935).
3. H. A. Frediani and L. Gamble, *Mikrochem. ver. Mikrochim. Acta*, **29**, 22-43 (1941).

**LITMUS**

Synonym: Lacmus

**Use:** Detection of ammonia.

Litmus is the blue coloring matter obtained from various species of lichens. It consists chiefly of azolitmin and erythrolitmin combined with alkalies.

It is obtained as a blue powder or as lumps or cubes which are partially soluble in water or alcohol.

**Detection of ammonia.** When red litmus is moistened with water and exposed to ammonia gas, the color of the dye changes to blue. This reaction has been used by Feigl<sup>1</sup> as a very sensitive reaction for the detection of small quantities of ammonia. With special apparatus and technique, Feigl states that 0.01γ of ammonia can be detected at a dilution of 1:5,000,000.

1. F. Feigl, *Mikrochemie*, **13**, 129-35 (1933).

**LOKAONIC ACID**

Synonym: Chinese green, locain, locao

**Use:** Detection of barium, lead, and potassium.

Lokaonic acid is a blue substance obtained from the bark of certain species of plants. It contains the glucoside rhamnucoside. The compound is insoluble in



water, alcohol, ether, chloroform, and benzene. It is soluble in dilute ammonia and sodium hydroxide.

**Preparation:** Treat Chinese green with a saturated solution of ammonium carbonate, filter, and add 90 per cent ethyl alcohol. Allow the mixture to stand 3 hours, filter, and wash the residue with 70 per cent alcohol until the filtrate is colorless. Dry at 50° C. and pulverize the blue-black mass. Repeat the above treatment and crystallize from ammonia. Dissolve the ammonium salt of lokaonic acid in water and oxalic acid. Wash and dry the precipitate at 100° C.

**Detection of barium.** An ammoniacal solution of lokaonic acid reacts with solutions of barium salts to give a blue precipitate. Lead and potassium give the same reaction.<sup>1-4</sup>

**Detection of lead.** Lead reacts with lokaonic acid in an ammoniacal solution to yield a blue precipitate.<sup>1,2</sup> Lead and barium give the same reaction, but these metals may be separated with the aid of sulfuric acid.

**Detection of potassium.** Lokaonic acid in an ammoniacal solution gives a blue color or precipitate when added to a solution of a potassium salt containing alcohol and potassium hydroxide.<sup>1-4</sup>

1. R. Kayser, *Ber.* **18**, 3417 (1885).
2. G. Gutzeit, *Helv. Chim. Acta.* **12**, 728 (1929).
3. M. Chambers, *Chemist-Analyst.* **27**, No. 1, 8 (1938); **32**, 2048 (1938).
4. F. Feigl, *Mikrochemie.* **8**, 356 (1930).

## OIL OF CLOVE

**Use:** Detection of ammonia.

Oil of clove is a volatile oil obtained from the dried flower buds of certain species of plants. It consists of 82-87 per cent eugenol, including about 10 per cent acetyleugenol, caryophyllene, small quantities of furfural, vanillin, and methylamylketone.

Clove oil is a colorless to pale yellow liquid, which becomes darker and thicker with age. Its sp. gr. is 1.038-1.060. It boils at about 250° C. It is almost insoluble in water, soluble in 2 volumes of 70 per cent alcohol, and very soluble in stronger alcohol, ether, and glacial acetic acid. It should be stored in a cool, dark place and in a well-stoppered bottle.

**Detection of ammonia.** Clove oil has been used in place of formaldehyde with silver nitrate for the detection of ammonia by the formation of a silver mirror, although with less satisfactory results.<sup>1</sup>

**Detection of potassium.** Tzoni<sup>2</sup> reports that potassium forms a crystalline precipitate with clove oil which may be used for the microchemical detection of potassium salts. The reaction is not sensitive, however, and is not recommended.

1. C. Duval, *Compt. rend.* **211**, 588-90 (1940); *C.A.* **36**, 365 (1942).
2. H. Tzoni, *Mikrochemie.* **19**, 208 (1935-36); *C.A.* **30**, 4623 (1936).

## SANDARAC RESIN

Sandarac resin contains about 80 per cent pimelic acid, about 10 per cent callitric and sandaracinic acid. It is a light yellow, brittle material. It is insoluble in water and benzene, but is soluble in ether, alcohol, acetone and hot caustic alkalis.

**Detection of aluminum.** Sandarac resin is used with purpurin in a sensitive test for aluminum. For details of this test, see section on purpurin (page 452).

1. K. Kershner and R. D. Duff, *J. Chem. Ed.* **9**, 1271 (1932); *C.A.* **26**, 4007 (1932).

## SAPONIN

**Use:** Detection of nitrate.

The saponins are a group of closely related glucosidal materials which are found in plants. Commercial saponin, which is usually obtained from *Quillaja* bark or from soap-root is a white to brownish amorphous powder. It is soluble in water, but is only slightly soluble in ethyl alcohol. It is insoluble in ether.

**Detection of nitrate.** Pure commercial saponin may be used to replace brucine or strychnine in the well-known test for nitrates. A blood-red color is obtained when a drop of concentrated sulfuric acid is added to a mixture of a nitrate and a small quantity of saponin.<sup>1</sup>

1. C. A. Mitchell, *Analyst.* **51**, 181 (1926); *C.A.* **20**, 2631 (1926).

## SHELLAC

**Use:** Determination of copper.

Shellac is a resinous product obtained from the bark of various species of trees. It is an exudation caused by the puncture of the insect *Coccus Lacca*.

**Determination of copper.** In the iodometric determination of copper, the blue iodo-starch is carried down by the precipitated cuprous iodide and tends to render the end-point of the titration indistinct.

Caldwell<sup>1</sup> has found that 0.5-1.0 ml. of a 4 per cent solution of white shellac in alcohol eliminates this difficulty. The shellac appears to deactivate the surface of the precipitate, and thus reduces adsorption of the blue compound.

1. J. R. Caldwell, *J. Am. Chem. Soc.* **57**, 96-7 (1935); *C.A.* **29**, 1738 (1935).

## SODIUM SULFORICINATE

**Use:** Determination of calcium and magnesium.

Sodium sulforicinate consists of a mixture of the sodium salts of the sulfonated acids of castor oil. It is a clear yellowish-brown syrupy liquid having a specific gravity of about 1.03. The liquid has an alkaline reaction. It is soluble in alcohol,

chloroform and ether. On shaking with water it foams strongly and yields an emulsion.

**Determination of calcium.** Calcium may be determined by the turbidity which is produced when a solution of a calcium salt is treated with sodium sulforicinate.<sup>1-3</sup> Magnesium does not produce a turbidity in the presence of the ammonium ion.<sup>2</sup> This makes possible the determination of calcium in the presence of magnesium without a preliminary separation. In 50 per cent alcohol, calcium and magnesium can be determined together by precipitation with ammonium ferrocyanide. After these ions have been determined together, the calcium alone may be determined by precipitation with sodium sulforicinate.<sup>3</sup>

Rona and Kleinmann<sup>1,4</sup> have used sodium sulforicinate for the determination of calcium in organic matter:

**Reagents.** *Sodium sulforicinate reagent:* Transfer 10 ml. of sodium sulforicinate (listed by Merck as sulforicinate-Berlioz-Heryng) to a graduated cylinder and add 112 ml. of 1 N sodium hydroxide. Dilute the mixture to 125 ml. with distilled water, and stir vigorously until the solution is clear and homogeneous.

*Standard calcium solution:* Transfer 0.4995 g. of pure dry calcium carbonate to a 100-ml. beaker and cover with distilled water. Then add 23.0 ml. of 1 N hydrochloric acid. The beaker should be covered during the addition of the acid to prevent loss of calcium. When solution is complete, rinse into a 2-liter graduated flask, and dilute to the mark with distilled water. This solution contains 0.1 mg. of calcium per ml.

**Procedure.** Ash the organic matter by first drying on a water-bath, then heating in an oven at 100° C. until completely dry, and finally ash with a Bunsen burner.

From 0.04 to 0.4 mg. of calcium is necessary for the determination. If the sample contains no more than this quantity of calcium, treat the ash with 4-5 drops of 1 N hydrochloric acid and with a micro-pipet transfer the solution to a glass stoppered 50-ml. flask which has a mark indicating 5 ml. and one indicating 25 ml. Treat the ash with an equal volume of hydrochloric acid and repeat the process. Finally rinse the pipet and the vessel containing the ash with 2-3 ml. of distilled water and transfer the washings to the flask. Dilute to 5 ml. with distilled water, and add to the solution the same number of drops of 1 N ammonium hydroxide as 1 N hydrochloric acid was used in dissolving the ash. Use the same pipet in order that the drops will have the same size. Do not use more than 0.5 ml. of hydrochloric acid or 0.6 ml. of ammonium hydroxide.

If the quantity of calcium present is such that not all of the ash is used, dissolve in a correspondingly greater quantity of acid, dilute to a definite volume with distilled water, and use a suitable aliquot for the analysis. The volume used should not contain more than 0.5-0.6 ml. of 1 N ammonium chloride.

To the 5 ml. of test solution add 0.4 ml. of the clear filtered reagent. The quantity of reagent must be accurately measured. Treat the standard solution

in the same manner and at as nearly the same time as possible. Let the mixture stand for 3 minutes for the turbidity to develop, then dilute to 25 ml. with distilled water and compare in a nephelometer within 30 minutes.

Calcium may be determined by this method with an error of about 1 per cent. The determination is very convenient and requires only a few minutes for completion.

In the analysis of blood, iron should be removed by the addition of a slight excess of ammonium hydroxide to the acid solution of the ash. The precipitated iron is removed by filtration.

1. P. Rona and H. Kleinmann, *Biochem. Z.* **137**, 157 (1923).
2. L. Kriss, *Biochem. Z.* **158**, 203-4 (1925); *C.A.* **19**, 3442 (1925).
3. L. Kriss, *Biochem. Z.* **162**, 359-65 (1925); *C.A.* **20**, 1772 (1926).
4. J. H. Yoe, *Photometric Chemical Analysis*, Vol. II, p. 125-8, John Wiley, New York (1929).

## SODIUM TAUROGLYCOCHOLATE

The addition of a very little sodium tauroglycocholate prevents the precipitate formed when 8-hydroxyquinoline is added to solutions of magnesium salts from adhering strongly to the sides of the beaker.<sup>1,2</sup>

1. C. C. Miller and I. C. McLennan, *J. Chem. Soc.* 656-9 (1940); *C.A.* **34**, 5370 (1940).
2. Hopkin and Williams, *Organic Reagents for Metals*, Third Edition, p. 67, Hopkin and Williams, Ltd., London (1938).

## UROBILIN

**Use:** Detection of copper, mercury, and zinc.

Determination of copper and zinc.

**Preparation:** Urobilin is not synthesized directly but is obtained from urine by the following procedure: Add acetic acid to several liters of urine containing considerable urobilin until the mixture is strongly acid, and then extract several times with small quantities of chloroform until the fractions no longer show a greenish fluorescence with zinc acetate. Shake the emulsified portion with talc and filter with suction. Repeatedly extract the chloroform solution with distilled water, which removes a considerable portion of the urobilin while mesobiliviolin and other impurities remain in the chloroform layer. Acidify the aqueous solution with hydrochloric acid, and again extract the resulting urobilin hydrochloride with chloroform. Extract the chloroform with 25 per cent hydrochloric acid, which is in turn diluted to 8 per cent, and again shaken out with chloroform. Dry the chloroform extract over anhydrous sodium sulfate, concentrate to a small volume, and pour into a large volume of petroleum ether. Redissolve the precipitated urobilin hydrochloride in chloroform and again precipitate with petroleum ether. Finally dissolve in hot chloroform and recrystallize by cooling. Repeat the crystallization from hot chloroform. The product does not melt sharply, but decomposes between 110-30° C.

Best results are obtained by using urine from patients having cardiac failure.<sup>1</sup>

Terwen<sup>2</sup> suggests preparing the urobilin by oxidizing a petroleum ether solution of urobilinogen with air by shaking and exposing to light.

**Detection and determination of zinc.** Jaffe<sup>3</sup> first observed that a greenish fluorescence is obtained when a solution of a zinc salt is treated with urobilin. This reaction was used by Roman and Delluc<sup>4,5</sup> for the detection of urobilin in urine, and for the detection of zinc. The reagent suggested is a urobilin solution obtained by shaking out with chloroform the urine of patients having hepatic disease.

**Procedure.** Mix 2 ml. of the chloroform extract with 5 ml. of absolute alcohol, and add a few drops of the neutral solution to be tested. An immediate green fluorescence develops if zinc is present.

Gutzeit<sup>6</sup> has used a similar procedure, but Wenger and co-workers<sup>7</sup> do not recommend this reagent because of the cost and difficulty of obtaining it.

Lutz<sup>8,14</sup> and Fairhall<sup>9</sup> have used the greenish fluorescence obtained by adding urobilin to a solution of a zinc salt for the colorimetric determination of small quantities of zinc. The color obtained with 0.001 mg. of this metal can be detected with the aid of a strong arc-light and an ultra-violet filter. Above 0.01 mg. of zinc the fluorescence is too strong for a colorimetric determination, but within the range of 0.001-0.01 mg. zinc may be determined with an accuracy of about 10 per cent.

The following procedure is used for determining zinc in organic matter:

**Reagent.** As reagent use a solution of urobilin in purified ethyl alcohol. The concentration of this solution need not be known exactly, but it should have a zinc equivalent of approximately 0.015 mg. per ml.

**Procedure.** Dry and then ignite the organic matter at a temperature not exceeding 550° C., and when the ash is gray or white, treat with 1 ml. of 6 N hydrochloric acid. If carbon is left in the residue, again ash after adding a little potassium nitrate, and again extract. Filter and wash the residue, and then treat the extract (or combined extracts) and washings with an excess of bromine water to oxidize iron, and then boil to remove the excess bromine. Dilute the mixture to 10-20 ml., and add a 10 per cent ammonium acetate solution dropwise until the mixture is neutral to methyl orange. Filter to remove the precipitated iron phosphate and wash well. If a large precipitate is obtained, dissolve in the smallest possible quantity of 6 N hydrochloric acid and dilute to 10-20 ml. Again neutralize to methyl orange with 10 per cent ammonium acetate solution, and reprecipitate by adding an excess of phosphate.

To the combined filtrates, which are neutral to methyl orange, add 0.5 mg. of copper from a standard copper sulfate solution, and then pass hydrogen sulfide through the mixture until all copper and zinc are precipitated. Filter, transfer the filter to the flask in which the sulfides were originally precipitated, add 0.2-0.5 ml. of 6 N nitric acid and heat almost to boiling with agitation. Filter the zinc-copper solution and wash the filter.

If large amounts of calcium and magnesium were present in the original sample, add 10 per cent sodium acetate to the nitric acid solution until neutral to methyl orange, and again precipitate and dissolve the sulfides as described above.

Evaporate the solution of copper and zinc nitrates just to dryness, and dissolve the residue in 6 N hydrochloric acid. Again evaporate to dryness to expel the nitric acid, and then repeat the entire process. Dissolve the chlorides of copper and zinc in 0.2 ml. of 6 N hydrochloric acid and dilute with 5 ml. of water. Pass hydrogen sulfide through the mixture to precipitate copper sulfide, which is then removed by filtration. Wash the filter, and then evaporate the filtrate and washings almost to dryness. Dilute to a known volume and use this solution for the final determination.

To a volume of this solution which should contain 0.001-0.01 mg. of zinc, and also to a series of standards prepared from a solution containing 0.01 mg. of zinc per ml., add sufficient urobilin solution to give a pink color. This is usually about 1 ml. Avoid an excess of the reagent, since this decreases the sensitivity of the test. Dilute both unknown and standard solution to 50 ml. with purified alcohol and mix well. To each add a drop of concentrated ammonium hydroxide and allow to stand for 10 minutes before making the color comparison. The solutions must not be compared after standing more than 30 minutes.

Copper, calcium, nickel, cobalt, magnesium, sodium and potassium interfere if present in quantities equal to that of zinc. The presence of cadmium serves to increase the color. The alcohol used in this determination must be highly purified.

**Detection and determination of copper.** A 1:1,000 solution of urobilin reacts with a dilute neutral solution of a copper salt to give a color ranging from rose-red to purple.<sup>10,11,15</sup> A rose color is given with a copper solution having a concentration of 1:1,000,000. The test is somewhat less sensitive in an acid solution, and if the acidity is due to the presence of a mineral acid, a little sodium acetate should be added after neutralization. The test is simply carried out by adding 10-20 drops of the reagent to 10 ml. of the neutral solution to be tested.

The test is unaffected by the presence of the sulfates or chlorides of aluminum, barium, calcium, cadmium, cobalt, stannous tin, beryllium, lithium, manganese, nickel, gold, platinum, strontium, zinc or ferrous iron, although the presence of the latter causes an intensification of the color. Silver nitrate, sodium arsenate, arsenite, molybdate or tungstate or ammonium vanadate do not affect the reaction. A greenish fluorescence is obtained if zinc is present.

Urobilin reacts with copper salts in the presence of ammonia to give colors ranging from yellow to red. This color reaction can be used for determining quantities of copper ranging from 0.0001-0.01 mg. of copper. The following procedure for determining copper in organic matter has been used by Emmerie:<sup>12</sup>

**Reagents. Urobilin solution:** Dissolve 5 mg. of urobilin in 100 ml. of re-distilled alcohol.

**Standard copper solution:** Dissolve 0.3928 g. of pure copper sulfate,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , in water and dilute to 1 liter. This solution contains 0.1 mg. of copper per ml. Dilute 5 ml. of this solution to 100 ml. The diluted solution contains 0.005 mg. of copper per ml.

**Procedure.** Ash the sample and dissolve the ash in 1:2 nitric acid. Add an excess of sulfuric acid and evaporate to the appearance of sulfur trioxide. Dilute with water and separate the copper electrolytically. Dissolve the copper in the smallest quantity of 1:1 nitric acid, add 1 drop of 0.1 N sulfuric acid and evaporate to remove the nitric acid. Dissolve the residue in 1 ml. of distilled water.

To this solution, which should be contained in a small vial, add 1 drop of 10 per cent ammonium hydroxide and 0.4 ml. of the urobilin solution. Dilute to 2 ml., and compare the resulting color with that of standards similarly prepared.

Silver and gold do not interfere with the above determination. Mercury does, however, and when present, the above procedure should be modified as follows:

**Procedure.** If mercury is present, add 1 drop of 1 per cent potassium iodide solution to the acid solution. Dissolve the precipitate of mercuric iodide with 0.2 ml. of 1 per cent sodium thiosulfate solution and then add ammonia and the reagent solution. Add the same quantities of potassium iodide and sodium thiosulfate to the standards which are used for the comparison.

**Detection of mercury.** A rose color is obtained when urobilin is added to solutions containing mercury salts. This reaction may be used for the detection of small quantities of mercury.<sup>13</sup> The rose color, which is extractable with chloroform, may be observed in solutions containing as little as 0.001 mg. of mercury.

1. J. J. Watson, *Proc. Soc. Expt. Biol. and Med.* **30**, 1210-11 (1932-33).
2. A. J. L. Terwen, *Nederland. Tijdschr. Geneeskunde*, **69**, I, 2492-507 (1925); *C.A.* **19**, 3501 (1925).
3. M. Jaffe, *Virchow's Archiv. f. pathol. Anatom.* **47**, 405 (1869).
4. Th. Roman and G. Delluc, *J. pharm. chim.* [6] **12**, 49-50 (1900).
5. Th. Roman and G. Delluc, *J. pharm. chim.* [6] **12**, 265 (1900).
6. G. Gutzeit, *Helv. Chim. Acta.* **12**, 713, 829 (1929).
7. P. Wenger, R. Duckert and D. Rieth, *Helv. Chim. Acta.* **25**, 406-15 (1942); *C.A.* **36**, 6438 (1942).
8. R. E. Lutz, *J. Ind. Hyg.* **7**, 273-89 (1925); *C.A.* **19**, 2614 (1925).
9. L. T. Fairhall, *J. Ind. Hyg.* **8**, 165, 528 (1926).
10. G. Bertrand and L. de Saint-Rat, *Compt. rend.* **203**, 140-3 (1936); *C.A.* **30**, 6304 (1936).
11. G. Bertrand and L. de Saint-Rat, *Mikrochim. Acta.* **1**, 5-8 (1937); *C.A.* **31**, 5711 (1937).
12. A. Emmerie, *Chem. Weekblad.* **27**, 552-4 (1930); *C.A.* **25**, 980 (1931).
13. C. A. Sagastume and V. Oliva, *Rev. facultad cienc. quim. (Univ. nac. La Plata)*, **12**, 43-5 (1937); *C.A.* **33**, 2436 (1939).
14. M. Haitinger, *Mikrochemie.* **16**, 321-56 (1934); *C.A.* **29**, 2470 (1935).
15. R. H. Muller and A. T. Burtzell, *Mikrochem. ver. Mikrochim. Acta.* **28**, 209-28 (1940).

## CHAPTER XIII

### MISCELLANEOUS COMPOUNDS

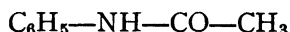
In this chapter are listed a number of structurally dissimilar organic compounds which cannot properly be included in any of the preceding sections.

#### ACETANILIDE

$C_8H_9ON$

Mol. Wt. 135.16

Beil. Ref. XII, 237



**Use:** Detection of cerium, chromium, ferricyanide, lead, manganese, oxidizing agents, nitrate and nitrite.

Acetanilide consists of lustrous, crystalline scales or a white powder. It melts at 113-115° C. It is only slightly soluble in water, but is more soluble in alcohol, chloroform, ether and acetone.

**Preparation:** Place 20 ml. of aniline and 24 ml. of glacial acetic acid in a flask which is fitted with a long, air-cooled reflux condenser. Boil gently for 5-6 hours. Pour the hot reaction mixture into 350 ml. of water which is vigorously stirred. Filter and wash the precipitate with cold water. Recrystallize from hot water to which a little decolorizing charcoal has been added. Filter hot through a large fluted filter. Cool the filtrate rapidly and filter with suction. Spread the crystals on paper to dry.

**Detection of oxidizing agents.** Various oxidizing agents, such as dichromate, lead peroxide, ferricyanide, permanganate, ceric salts and nitrites and nitrates cause color changes with acetanilide, which may be used for the detection of the former. The colors are at first some shade of red, and these then fade or otherwise change. A solution of the reagent in sulfuric acid can be used as the reagent, or the solid may be added to a sulfuric acid solution of the material to be tested.<sup>1,2</sup>

1. W. Lenz, *Z. anal. Chem.* **35**, 121 (1896).

2. I. M. Korenman, *Z. anal. Chem.* **93**, 438-47 (1933).

#### ACETOMERCURITHYMOLSULFONIC ACID

**Use:** Standard in iodometry.

**Standard in iodometry.** Bordeianu and co-workers<sup>1</sup> have proposed the use of acetomercurithymolsulfonic acid for the standardization of solutions of iodine. The compound is readily obtainable in a very pure state and has a high molecular weight. It reacts with iodine with the displacement of the aceto-



mercuric group, and the end-point may be obtained with starch. Results obtained using this reagent are said to be more accurate than those employing arsenous oxide.

1. C. V. Bordeianu, I. N. Petrescu and L. Staicovici, *Bul. Soc. Stiinte Farm. Romania*. **4**, 473-85 (1939); *Chimie et industrie*. **43**, 458; *C.A.* **34**, 4356 (1940).

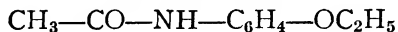
## ACETOPHENETIDE

Synonym: Ethoxyacetanilide, acetophenetidine and phenacetin

$C_{10}H_{13}O_2N$

Mol. Wt. 179.11

Beil. Ref. XIII, 461



Acetophenetide is a white, odorless, slightly bitter compound. It occurs as crystals or scales which melt at  $134-5^\circ$ . It is only slightly soluble in cold, but more so in hot water. It is moderately soluble in alcohol and chloroform, slightly soluble in ether, and insoluble in glycerol.

**Preparation:** Mix 8 g. of aminoethoxybenzene with 30 ml. of water and add 8 g. of acetic anhydride. Shake vigorously and filter the crystalline compound which forms. Recrystallize from a mixture of equal parts of water and alcohol.<sup>1</sup>

Acetophenetide is a commonly used antipyretic and may easily be obtained from drug supply houses.

Solutions of cupferron (ammonium salt of nitrosophenylhydroxylamine) are comparatively unstable, particularly in sunlight, and may be used only for short periods before they become unsuited for analytical determinations. This constitutes a rather serious problem, particularly when the reagent is being extensively used in the analytical laboratory. Germuth<sup>2</sup> has found that the addition of 0.05 g. of acetophenetide to each 100 ml. of cupferron solution stabilizes the reagent to such an extent that after one month there is only slight decomposition. Many compounds have been used for this purpose, but acetophenetide is by far the most satisfactory.

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2. F. G. Germuth, *Chemist-Analyst*. **17**, 3-15 (1928); *C.A.* **22**, 3372 (1928).

## ALUMINUM ETHYLATE

Synonym: Aluminum ethoxide

$C_6H_{15}O_3Al$

Mol. Wt. 164.15

Beil. Ref. I, 313



**Use:** Detection of small quantities of water in organic liquids.

Aluminum ethylate is a solid melting at  $150-160^\circ$ . It decomposes with water and is only very slightly soluble in alcohol and ether.

**Preparation of reagent:** In a flask equipped with a reflux condenser place 27 g. of aluminum shavings, 276 g. of absolute alcohol, and 0.2 g. of mercury.

After the initial reaction has subsided, heat the mixture on a water bath for a few hours until the thick, gray precipitate of the reagent appears dry. Then distill from an oil bath at 210-220° C., and heat carefully the dark mass on a sand bath to 340° C. (thermometer in the melt). If, after 1 hour, the thermometer, in spite of further warming, has fallen to 330° C., discontinue the heating. Cool, dissolve the mass in 1 liter of boiling xylene, and then filter with suction through a dry paper. Use the clear liquid as the reagent.

**Detection of water.** Aluminum ethylate reacts with small quantities of water in organic liquids to form a voluminous precipitate of aluminum hydroxide. This serves to indicate the presence of water.

**Procedure for test.** Place a few ml. of the liquid to be tested in a test tube, and mix with a drop of the xylene solution of the reagent. Depending upon the quantity of water present, a voluminous precipitate forms immediately or after a few seconds.

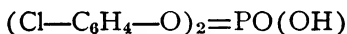
1. F. Henle, *Ber.* 53, 719 (1920).

### BIS-*p*-CHLOROPHENYLPHOSPHORIC ACID

$C_{12}H_9O_4Cl_2P$

Mol. Wt. 319.07

Beil. Ref. VI, 188



**Use:** Determination of iron.

Bis-*p*-chlorophenylphosphoric acid is a solid melting at 126-127° C. It is moderately soluble in hot water, alcohol, ether and chloroform. The sodium salt is soluble in alcohol, but only moderately soluble in cold water.

**Preparation:** Mix 88 g. of *p*-chlorophenol with 93 g. of phosphorus oxychloride and heat under reflux on a sand-bath at a gentle boil for 8 to 11 hours, or until hydrogen chloride is no longer evolved. Fractionally distill the product *in vacuo*. A small quantity of phosphorus oxychloride first distills, and at 142° C. at 11 mm. the *p*-chlorophenylphosphoric acid dichloride distills. When the temperature begins to fall, interrupt the distillation and add the warm contents of the flask to a 20 per cent sodium hydroxide solution with shaking, and warm one hour on a water-bath. Now add the calculated quantity of sodium hydroxide plus 5 per cent in excess (assuming that the flask contains only the monochloride). On cooling the sodium salt of bis-*p*-chlorophenylphosphoric acid separates. Cool the mixture in ice, filter and recrystallize from water.<sup>1,2</sup>

**Determination of iron.** Ammonium bis-*p*-chlorophenylphosphate precipitates ferric iron quantitatively from a solution that is 2 N in mineral acid. Zetzsche and Nachmann<sup>1</sup> have used this property of the reagent for the gravimetric determination of iron.

**Procedure.** Dilute a solution containing about 0.03 g. of iron to 150 ml. and add solid ammonium chloride so that after precipitation the concentration exceeds 1 per cent. About 3-4 g. of ammonium chloride is sufficient. Then add

25 ml. of concentrated hydrochloric acid and add dropwise and with stirring a 0.1 N solution of the sodium salt of the reagent until precipitation is complete. This is indicated when the supernatant liquid is colorless. About 25 ml. of the precipitant is necessary. Warm the mixture on a water-bath and after 30 minutes add one-sixth to one-fifth of the quantity of the reagent previously used in a thin stream, and warm an additional 30 minutes on the water bath. Place the beaker in cold water and allow to stand for one-half hour. Filter the yellow precipitate, and transfer to the filter with N hydrochloric acid. Wash with 100 ml. of N hydrochloric acid, and then 50 ml. of cold, and finally 100 ml. of hot water. Transfer the washed precipitate to the beaker with water and dilute to 100 ml. Add some ammonium chloride, warm to 70° C., and then add ammonium hydroxide with stirring. Allow to stand for 10 minutes on a water-bath, and filter the resulting ferric hydroxide. Wash, ash, ignite, and weigh as ferric oxide.

Aluminum, chromium, manganese, cobalt, nickel, zinc, copper, bismuth, cadmium, antimony, alkaline earths, arsenate and phosphate do not interfere, although a double precipitation may be necessary.

1. F. Zetzsche and M. Nachmann, *Helv. Chim. Acta*, 9, 420, 705 979 (1926).
2. W. Autenrieth, *Ber.* 30, 2375 (1897).

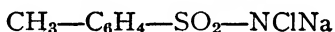
## CHLORAMINE T

Synonym: Sodium *p*-toluenesulfonchloramide, chlorazene, chloramine, chlorazone, activin



Mol. Wt. 245.66

Beil. Ref. XI, 107 (29)



**Use:** Detection of bromate and halogens.

Determination of iodides (and other substances which can be determined iodometrically), thallium and tin.

Chloramine T is a white or faintly yellow crystalline powder. It has a slight chlorine odor, and decomposes slowly on exposure to air. The compound is fairly soluble in water, but is insoluble in benzene, chloroform and ether. It is decomposed by alcohol.

**Preparation:** Dissolve 1 mole of *p*-toluenesulfonamidè in a warm, alkaline 1.3-2.0 N solution of sodium hypochlorite. For each mole of the amide, use 1.05-1.1 moles of sodium hypochlorite, and one mole of sodium hydroxide. Crystals of the reagent form when the mixture is cooled, and an additional quantity of the compound is obtained by evaporation. Dissolve the crude precipitate in twice its weight of hot water, and then cool rapidly without stirring. The recrystallization may be repeated if greater purity is desired.<sup>1</sup>

**Use of chloramine T in titrimetric analysis.** Aqueous solutions of chloramine T, contain some sodium hypochlorite, which is formed by hydrolysis, but

solutions of the reagent are stable if protected from light. Chloramine T solutions may, therefore, be used to replace the more expensive iodine, and the less stable solutions of chlorine or sodium hypochlorite in many procedures in titrimetric analysis.<sup>2-4</sup> A few of these applications are listed as follows:

(a) Ferrocyanides are oxidized to ferricyanides with standard chloramine T, and the excess reagent determined by adding sodium bicarbonate, a little potassium iodide, and starch, and titrating with a standard sodium arsenite solution.<sup>6</sup>

(b) The thiocyanate ion is oxidized by chloramine T to cyanate and sulfate ions. Using this reaction, thiocyanates can be determined by titrating the excess reagent with a standard sodium arsenite solution.<sup>6</sup>

(c) Hydrazine is oxidized to nitrogen, and can be titrated directly with chloramine T after adding sodium bicarbonate, a little starch, and potassium iodide.<sup>6</sup>

(d) Hypophosphorus acid is oxidized to phosphorus acid by chloramine T in 0.24 N sulfuric acid. After allowing the mixture to stand 24 hours, the hypophosphorus acid can be determined by adding a little potassium iodide and titrating the excess reagent with standard thiosulfate solution.<sup>6</sup>

(e) Carbon disulfide is dissolved in 5 per cent potassium hydroxide in ethyl alcohol, and the potassium xanthate is oxidized with the aid of chloramine T according to the reaction of Gastine, page 100-101. This reaction is nearly quantitative. Thus chloramine T may be used to determine carbon disulfide.

(f) Arsenic, antimony, tin and iron may be titrated directly with chloramine T by adding a little potassium iodide and starch. The procedure is very similar to that employed in the iodometric determination of these elements.<sup>4</sup>

(g) Chloramine T is also recommended for the determination of nitrous acid and sulfites, because of its stability in aqueous solution, and its powerful oxidizing action.<sup>6</sup>

(h) Jangmichl and Hackl<sup>7</sup> have recommended chloramine T as especially suited for the analysis of sodium hydrosulfite.

Tomicek and Sucharda<sup>8,9</sup> and Herzog<sup>10</sup> have studied the use of chloramine T as an oxidizing agent in titrimetric analysis, and report that it is suitable for the potentiometric determination of trivalent arsenic and antimony, bivalent tin and iron, and ferrocyanide and iodide ions, and for the visual titration of trivalent antimony and arsenic, using methyl red as an indicator. In each instance the medium must be acid, preferably with hydrochloric acid. Suitable concentrations of hydrochloric acid for the above determinations are listed as follows:

Arsenic . . . . .	0.35 N or 1.75 N
Antimony . . . . .	1.0 N
Tin . . . . .	1.0 N
Ferrocyanide . . .	1.0 N
Iron . . . . .	2.4 N
Iodide . . . . .	0.35 N

When in the presence of reducing agents, chloramine T decomposes quantitatively into *p*-toluenesulfonamide, sodium chloride and oxygen. A solution of 15 g. of chloramine T in a liter of water gives a 0.1 N chlorine solution of great stability. Such solutions may be standardized against arsenious oxide, and are practically stable for periods as long as 3 months.

Lestra <sup>11</sup> reports that some confusion exists regarding the actual chlorine content of chloramine T and its oxidizing power expressed in chlorine equivalents.

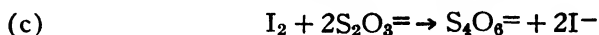
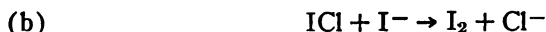
**Separation and detection of the halogens.** If a solution of chloramine T is added to a neutral solution containing the alkali halides, free iodine is precipitated and may be removed by filtration. The last traces of iodine are removed by boiling the filtrate. Bromine can then be detected by first adding a few drops of chloramine T and then several drops of concentrated hydrochloric acid. The test is made <sup>more</sup> sensitive by extracting the bromine with carbon disulfide, or carbon tetrachloride.<sup>12,13</sup> There are two distinct factors which may cause interference with the above test: The first of these occurs when the iodine is precipitated with chloramine T. As chloramine T decomposes, the solution becomes strongly alkaline with the result that some iodine remains in solution as sodium iodide, sodium hypoiodite and sodium iodate. This effect may be minimized by the addition of ammonium acetate. The second disturbance also occurs during precipitation of iodine, for, if too great an excess of chloramine T is added, some of the free iodine may be oxidized to iodic acid. This reaction can be controlled by adding chloramine T dropwise with constant stirring until the mixture becomes black, and then adding an additional few drops of the reagent.

**Determination of iodide.** Jonas <sup>14</sup> has used the following procedure for the determination of iodides.

**Reagent.** Dissolve 15 g. of chloramine T and 19 g. of sodium tetraborate in 1 liter of water.

**Procedure.** First oxidize the iodide to iodine chloride (ICl) in a 3 N hydrochloric acid solution by adding the chloramine T solution from a buret until the color of a few drops of carbon tetrachloride, which has been added, is no longer violet. Then dilute with water until the solution is 0.2-0.3 N in hydrochloric acid. Add an excess of potassium iodide, and titrate the liberated iodine with sodium thiosulfate. If ferric ions are present, 10 per cent disodium phosphate should be added before the final titration.

The titrations with chloramine T and sodium thiosulfate give two results, whose mean value gives an accurate estimate of the amount of iodide originally present. The following equations represent the changes occurring during the determination:



**Detection of bromate.** The following reaction may be used for detecting bromates: <sup>15,16</sup>

**Reagent.** Dissolve 0.1 g. of fluorescein in 5 ml. of 0.1 N sodium hydroxide solution and dilute to 1 liter.

**Procedure.** To 1 ml. of the solution to be tested, add 0.1 ml. of the fluorescein reagent, and a few crystals of oxalic acid. Heat to boiling, cool, and add 1-3 drops of 0.1 M chloramine T. Compare the color change with a blank solution similarly treated. The test can be obtained with as little as 10% of potassium bromate in the presence of 0.1 g. of potassium chlorate.

The addition of an alkali hydroxide destroys this test.

**Determination of bromine.** Chloramine T has been used for the oxidation of bromide to free bromine as a preliminary to the colorimetric determination of bromine with phenol red.<sup>22</sup> For the details of this procedure, see section on phenol red (page 546).

**Determination of thallium.** Thallous salts can be titrated with chloramine T in the presence of hydrochloric acid and potassium bromide.<sup>17,19</sup> The hypochlorous acid formed during the decomposition of chloramine T reacts with hydrochloric acid and potassium bromide to form free bromine, and this oxidizes univalent thallium to the trivalent state.

The following procedure may be used.

**Procedure.** To 10 ml. of approximately 0.1 N thallous nitrate solution, add 10 ml. of 10 per cent potassium bromide, 5 ml. of 2 N hydrochloric acid, and 35 ml. of water. Slowly titrate potentiometrically at room temperature with 0.1 N chloramine T solution. One mole of chloramine corresponds to 1 atom of thallium.

Results obtained by this method are within 2 per cent of the theoretical value.

**Determination of tin.** Tin, after reduction to the bivalent state with metallic iron, may be titrated with a solution of chloramine T.<sup>20,21</sup>

**Procedure.** To a slightly acid solution containing 0.05-0.15 g. of tin in a 300-ml. Erlenmeyer flask, add 30 ml. of 6 N hydrochloric acid and about 3 g. of clean iron filings. Close the flask with a stopper carrying a cut off separatory funnel which has been filled with 70 ml. of water containing 3 g. of sodium bicarbonate. Open the cock slightly so that when there is no pressure within the flask the liquid flows in at the rate of about 1 drop every 2 or 3 seconds. Heat carefully, and when all the iron has dissolved remove the flame, open the stop cock, and allow the flask and contents to cool to room temperature. Then add a little starch indicator and about 2 g. of potassium iodide. By opening and closing the stop cock from time to time, and applying gentle suction the sodium bicarbonate is caused to flow into the flask. The flask is held in an inclined position so that the liquid washes the walls of the vessel. Finally remove

the stopper and titrate with 0.1 N chloramine T. One ml. of 0.1 N chloramine solution = 5.935 mg. tin.

The unusual conditions of this reaction are necessary to prevent oxidation of the stannous tin by atmospheric oxygen.

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6. P. N. Van Eck, *Pharm. Weekblad.* **63**, 1117-21 (1926); *C.A.* **20**, 3660 (1926).
7. E. Jangmichl and J. Hackl, *Melliand Textilber.* **7**, 850-1 (1926); *C.A.* **21**, 2856 (1927).
8. O. Tomicek and B. Sucharda, *Casopis Ceskoslov. Lekarnictva.* **11**, 285-9, 309-20 (1931); *C.A.* **26**, 1210 (1932).
9. O. Tomicek and B. Sucharda, *Collection Czechoslov. Chem. Communications.* **4**, 285-99 (1932); *C.A.* **26**, 5868 (1932).
10. W. Herzog, *Oesterr. Chem.-Ztg.* **29**, 26-7 (1926).
11. H. Lestra, *Bull. sci. pharmacol.* **46**, 26-7 (1939); *C.A.* **33**, 3294 (1939).
12. E. M. Gerstenzang, *J. Chem. Ed.* **8**, 1187-9 (1931); *C.A.* **25**, 3272 (1931).
13. S. Sussman, *J. Chem. Ed.* **9**, 1652-3 (1932); *C.A.* **26**, 5273 (1932).
14. G. Jonas, *Magyar Gyogyszeresstud Tarsasag Ertesitoje.* **10**, 526-39 (1934); *C.A.* **29**, 1745 (1935).
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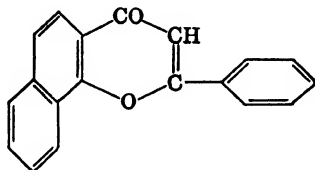
### $\alpha$ -NAPHTHOFLAVONE

Synonym : 7,8-Benzoflavone

$C_{19}H_{12}O_2$

Mol. Wt. 272.29

Beil. Ref. XVII, 390(216).

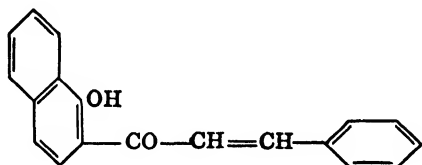


**Use:** Detection of bromine, chlorine, copper, gold, iodine, iron, platinum, selenium and tellurium.

Determination of chlorine and iodine.

$\alpha$ -Naphthoflavone consists of leaves or needles which melt at 154-156° C. It is soluble in ethyl alcohol and dissolves in concentrated sulfuric acid to yield a colorless solution with a greenish fluorescence.

**Preparation.** *Flavanone*: To 2 g. of the chalcone



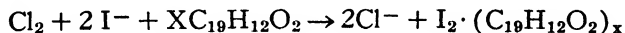
add sufficient alcohol so that at the boiling point solution is just complete. This requires about 120 ml. of alcohol. Mix the boiling solution with a second solution prepared from 16 ml. of concentrated hydrochloric acid and 48 ml. of water, and boil for 24 hours under reflux. Filter while hot from the residue, and rapidly boil this residue with alcoholic hydrogen chloride to recover more flavanone. Cool and filter off the crystals, and purify by recrystallizing from alcohol.

*$\alpha$ -Naphthoflavone*: To 0.5 g. of flavanone, add gradually with shaking 0.35 g. of bromine in a carbon disulfide solution. Evaporate the solution and press out the residue on a porous plate. Recrystallize from alcohol. To a boiling alcoholic solution add 40 per cent potassium hydroxide solution to the appearance of a turbidity and a change in color from yellow to red.  *$\alpha$ -Naphthoflavone* separates from this solution on cooling.<sup>1</sup>

**Detection and determination of iodine.**  *$\alpha$ -Naphthoflavone* reacts with free iodine to form a blue, water-insoluble complex, which may be used for the detection and the colorimetric determination of small quantities of iodine. According to Reith<sup>2</sup> the reaction is about five times as sensitive as that with starch, and may be used to detect as little as 0.005 mg. of free iodine in 100 ml. of solution. A one per cent alcoholic solution of the reagent is used for the iodine test.  *$\alpha$ -Naphthoflavone* may also be employed as an indicator in iodometry.

**Procedure.** Add 0.5 ml. of a 1 per cent alcoholic solution of  *$\alpha$ -naphthoflavone* to 100 ml. of a solution which has been made 0.1 N with sulfuric acid and titrate with 0.001 N sodium thiosulfate solution. In the absence of iodine, the initial color is blue and the end-point is colorless; with iodide the initial color is brown and the end-point is violet.

**Detection and determination of chlorine.** The reaction of  *$\alpha$ -naphthoflavone* with iodine has also been made the basis for a method for the detection and determination of free chlorine. Chlorine reacts with iodides to form free iodine, which immediately forms an adsorption complex according to the following equation:



Gilcreas and Hallinan<sup>3</sup> observed the influence of pH and iodide ion concentration on the accuracy of iodometric tests for residual chlorine in water, and devised a direct colorimetric technique in which  *$\alpha$ -naphthoflavone* is used as the indicator. This method has proved very valuable in routine control of chlorination processes in which the essential reactions are practically unaffected



by the quantities of nitrites, ferric iron and colloidal manganese dioxide which are likely to be present in the water. The method is influenced, however, by chlorine adsorption compounds, and by the presence of colored or turbid matter, as is also true of the well-known *o*-tolidine test.

Colored matter in water is usually in solution, and consequently may be separated by filtration from the water-insoluble iodide adsorption complex formed in the  $\alpha$ -naphthoflavone reaction. Sources of turbidity are usually insoluble in alcohol, which may be used to dissolve the adsorption compound. It also appears that iodine may be separated from interfering oxidizing substances, which are not likely to be insoluble in water and soluble in alcohol.

The following procedure is used by Hallinan<sup>4</sup> for the determination of residual chlorine in water and in highly colored sewages and trade wastes:

**Procedure.** To 50 ml. of a chlorine solution, add a dry mixture of 1 g. of potassium iodide and a suitable quantity of buffer. The buffers are selected to avoid calcium precipitation and unnecessary increase in the chlorine demand. For 1 liter of the sample, the following quantities of buffers were used: (a) pH 6.7, 20 g. of potassium sodium tartrate; (b) pH 8.9, 16 g. of sodium diethyl barbiturate, 3 g. of potassium sodium tartrate, and 1 g. of potassium hydrogen tartrate; (c) pH 10.0, 20 g. of sodium diethyl barbiturate.

Dissolve the iodide and buffer as rapidly as possible, and allow the mixture to stand for 2 minutes. Then add 0.5 ml. of a 0.2 per cent solution of  $\alpha$ -naphthoflavone in 95 per cent alcohol and mix well. Allow the mixture to stand for 3 minutes, and coagulate the adsorption compound by violent agitation. Filter immediately through a hard paper in a Gooch crucible with suction. Test the first portion of the clear filtrate for unadsorbed iodine with a fresh portion of  $\alpha$ -naphthoflavone solution. If any is found, discard the materials and repeat the procedure with a small portion of the sample which has been diluted to 50 ml. with chlorine-free water so that the  $\alpha$ -naphthoflavone reagent will be in excess. Wash the precipitate with about 2 ml. of chlorine-free water and discard the filtrate and washings. Dissolve the precipitate, wash the filter with about 5 ml. of 0.1 per cent alcoholic solution of potassium iodide.

TABLE 49.—PERMANENT COLOR STANDARDS FOR CHLORINE DETERMINATION

Chlorine in 50 ml. sample p.p.m.	Color solution ml.
0.00	0.08
0.05	0.38
0.10	0.70
0.20	1.30
0.30	1.91
0.40	2.52
0.50	3.15
0.60	3.78
0.80	5.00

Compare the yellow solution with permanent color standards prepared as follows: Dissolve 2.0 g. of potassium chloroplatinate,  $K_2PtCl_6$ ; 3.75 g. of copper sulfate,  $CuSO_4 \cdot 5H_2O$ ; 2.5 ml. of concentrated sulfuric acid, and 100 ml. of concentrated hydrochloric acid in distilled water and dilute to 1 liter. The chlorine equivalents in a 50-ml. sample of solution, prepared by diluting different quantities of the standard to 5 ml. with distilled water, are given in Table 49.

The color comparison is best carried out by viewing solutions longitudinally in flat-bottom, shell vials having an outside diameter of 13 m.m. Use north light reflected from a white matte surface. The values given in Table 49 should be compared with chlorine standards and modified or simply recalibrated as necessary for a particular technique and reagent. The values given are for solutions of pH 6.7.

Hahn and co-workers<sup>5</sup> have used a 0.1 per cent alcoholic solution of  $\alpha$ -naphthoflavone for the determination of free chlorine in potable water. The procedure depends upon the blue color which appears when an iodide is added to a solution containing free chlorine and  $\alpha$ -naphthoflavone, and upon the subsequent change of this color to pink upon titration with a solution of sodium thiosulfate.

This reaction has also been studied by Rokita.<sup>11</sup>

**Detection of bromine.**  $\alpha$ -Naphthoflavone reacts with iodine to form an insoluble blue-violet compound, and with bromine to form an orange-red compound. Both of these elements may be detected by their respective color reactions. Bromides may be detected after the liberation of bromine by means of a suitable oxidizing agent. In the presence of iodides, the iodine, which is also formed by oxidation, is first precipitated as the naphthoflavone compound; but this is decomposed on further treatment with the oxidizing agent to form iodic acid. Free chlorine does not react with  $\alpha$ -naphthoflavone and so chlorides do not interfere. The following procedure, in which permolybdic acid is used as the oxidizing agent, is recommended by Ozel.<sup>8-10</sup>

**Procedure.** Place a drop of the solution to be tested on a spot plate and add a small quantity of solid molybdic acid,  $H_2MoO_4$ . Then add a drop of a 0.1 per cent solution of  $\alpha$ -naphthoflavone in glacial acetic acid, and finally 1-2 drops of a mixture of 3 parts of 50 per cent sulfuric acid and 1 part of 30 per cent hydrogen peroxide. An orange color appears if bromide is present. The reaction is sensitive to 1 $\gamma$  of bromine at a dilution of 1:50,000.

With the above procedure 0.5 $\gamma$  of bromide may be detected in the presence of iodides if the latter are first decomposed by the addition of an excess of permolybdic acid. This test may be carried out in a saturated sodium chloride solution.

**Fluorescence analysis.**  $\alpha$ -Naphthoflavone exhibits a fluorescence when viewed under ultra-violet light, but the iodine adsorption complex does not fluoresce under similar conditions. Goto<sup>6,7</sup> has used this reaction for the detection of copper, platinum, gold, selenium, tellurium and iron. When a cupric salt is treated with potassium iodide in the presence of  $\alpha$ -naphthoflavone and un-

der ultra-violet light, the fluorescence disappears due to the liberation of free iodine in the reaction with the cupric ion. In this way as little as 0.5γ of copper can be detected. Many substances which oxidize iodide to free iodine interfere by giving a similar test.

α-Naphthoflavone and potassium iodide yield a fluorescence which is destroyed by the addition of as little as 5γ of platinum. Gold, selenium and tellurium are detected in a similar manner. As little as 0.25γ of ferric iron can also be detected with the α-naphthoflavone-potassium iodide reagent.

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5. M. Hahn, F. Schutze and S. Pavildes, *Z. Hyg. Infektionskrankh.* **108**, 450 (1928); *C.A.* **22**, 3716 (1928).
6. H. Goto, *J. Chem. Soc. Japan.* **59**, 547-54 (1938); *C.A.* **32**, 5721 (1938).
7. H. Goto, *Science Repts. Tohoku Imp. Univ. First. Ser.* **29**, 204-18 (1940); *C.A.* **35**, 1720-23 (1941).
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9. R. Uzel, *Coll. Trav. chim. Tcheslovaquie.* **7**, 380-7 (1935).
10. F. Schulek, *Z. anal. Chem.* **111**, 102 (1935).
11. W. Rokita, *Brauer-Hofen-Ztg. Gambrinus* **56**, 346 (1929); *Dept. Sci. Ind. Research, Water Pollution Research, Summary of Current Literature.* **3**, 184 (1930).

### α-NAPHTHOXYDICHLOROPHOSPHINE

$C_{10}H_7OPCl_2$

Mol. Wt. 245.10

Beil. Ref. VI, 610.

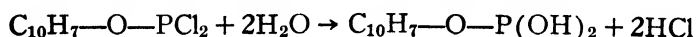
$C_{10}H_7-O-PCl_2$

**Use:** Determination of water.

α-Naphthoxydichlorophosphine is a colorless non-fuming liquid. It boils at 180° C. at 18 mm. of pressure, and has a sp. gr. of 1.0776. It dissolves in absolute alcohol and anhydrous ether.

**Preparation:** Place 60 g. of α-naphthol and 200 g. of phosphorus trichloride in a flask which is fitted with a reflux condenser. Close the reflux condenser with a calcium chloride tube. Warm the mixture gently for 20-24 hours until the evolution of hydrogen chloride has practically ceased. Then fractionally distill the clear mixture to remove the phosphorus trichloride (B.P. = 150° C.), and then distill the α-naphthoxydichlorophosphine under reduced pressure. Collect the fraction boiling at 174-176° C. at 15 mm. of pressure. Remove traces of phosphorus trichloride by heating the liquid to 100° C. in a current of air which has been dried with phosphorus pentoxide.<sup>1</sup>

**Determination of water in organic liquids.** α-Naphthoxydichlorophosphine reacts with water according to the following equation:



This reaction has been used by Bell<sup>2</sup> for the determination of water in organic liquids. The hydrogen chloride produced in the above reaction is removed from the reaction mixture by a current of dry air, absorbed in water, and then titrated with a standard base. The reagent is dissolved in a suitable solvent such as benzene or bromobenzene. The sample to be analyzed is then added to this solution, and a current of dry air is passed through the mixture. The gas is dried over  $P_2O_5$  and absorbed in water. The water in the sample is finally determined indirectly by titrating the absorbed hydrochloric acid, and calculating the amount of water present from the above equation.

1. P. Kunz, *Ber.* 27, 2560 (1894).
2. R. P. Bell, *J. Chem. Soc.* 135, 2903 (1932).

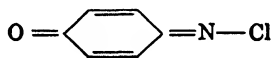
### QUINONECHLORIMIDE

$C_6H_4ONCl$

Mol. Wt. 141.56

Beil. Ref. VII, 619 (344).

**Use:** Detection of ferrocyanide.



The reagent is a yellow, crystalline compound with a quinoline-like odor. It melts at  $86^\circ C.$ , although it decomposes explosively at high temperatures. It is only slightly soluble in cold, but is readily soluble in hot water. It also dissolves in alcohol, ether, benzene, acetic acid, and chloroform.

**Preparation:** Dissolve 43 g. of *p*-aminophenol hydrochloride in 100 ml. of concentrated hydrochloric acid and 500 g. of water, and add slowly with vigorous shaking, and with very careful cooling, to a solution of sodium hypochlorite prepared from 45 g. of sodium hydroxide and 35 g. of chlorine. The yield is almost quantitative. Crystallize the product from gasoline.<sup>1</sup>

**Detection of ferrocyanide.** Quinonechlorimide may be used as a reagent for the detection of ferrocyanides, with which it reacts to yield an emerald-green color or dark brown precipitate, depending on the amount of ferrocyanide present.<sup>2</sup>

**Procedure.** Place 0.5 ml. of a slightly acid solution to be tested on a white spot plate, and add 5 drops of a 0.5 per cent solution of quinonechlorimide in ethyl alcohol. An emerald-green color develops within 15-30 seconds if ferrocyanides are present. Strong oxidizing agents interfere, but ferricyanide does not.<sup>2</sup> As little as 5γ of  $K_4Fe(CN)_6 \cdot 3H_2O$  gives this test.

1. R. Willstätter and E. Mayer, *Ber.* 37, 1499 (1904).
2. E. W. Blank, *J. Chem. Ed.* 19, 321 (1942); *C.A.* 36, 5111 (1942).

**TETRAPHENYLARSONIUM CHLORIDE** $C_{24}H_{20}AsCl \cdot 2H_2O$ 

Mol. Wt. 454.56

 $(C_6H_5)_4AsCl$ 

**Use:** Determination of cadmium, chlorate, iodate, manganese, mercury, rhenium, tin, and zinc.

Tetraphenylarsonium chloride is a white crystalline solid. It is formed as the dihydrate, but loses its water of hydration at 100° C. It melts at 258-60° C. It is freely soluble in water, and is also soluble in alcohol and methyl alcohol, but is only sparingly soluble in acetone.

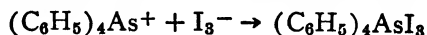
**Preparation.** *Tetraphenylarsonium bromide:* Prepare phenyl magnesium bromide from 2.4 g. of magnesium, 10.5 ml. of bromobenzene and 60 ml. of ether in a 3-necked flask, which is fitted with a reflux condenser and a stirrer with a mercury seal. Stir vigorously and add rapidly 12 g. of triphenylarsine oxide dissolved in 25 ml. of hot dry benzene. Stir for 30 minutes and remove the benzene ether layer by decantation, and triturate the solid with 40 ml. of water. Add 75 ml. of constant boiling hydrobromic acid, and immediately pour the mixture into a beaker. Crystals of tetraphenylarsonium bromide begin to separate. Allow the mixture to stand and filter off the crystals. Wash thoroughly with benzene and recrystallize from water to which decolorizing charcoal has been added.

*Tetraphenylarsonium chloride:* Recrystallize 5 g. of the tetraphenylarsonium bromide 3 times from a hot mixture of 15 ml. of concentrated hydrochloric acid and 5 ml. of water. Dissolve in hot water and boil with a little charcoal. Filter, neutralize the filtrate with sodium carbonate, and evaporate to dryness. Extract with absolute alcohol, remove the alcohol from the extract, and rub the residue under absolute ether. Dissolve in the least possible quantity of absolute alcohol or ethyl acetate, and precipitate by the addition of ether.<sup>1,2</sup>

**Analytical reactions.** In aqueous solution, tetraphenylarsonium chloride is a strong electrolyte which yields tetraphenylarsonium,  $(C_6H_5)_4As^+$ , and chloride ions.<sup>2</sup> The tetraphenylarsonium cation forms insoluble salts with a number of anions, such as perrhenate, permanganate, perchlorate and periodate, and these salts can be isolated and weighed.

Mercury, tin, zinc and cadmium are also precipitated quantitatively with tetraphenylarsonium chloride, and the excess of the latter can then be titrated iodometrically. These reactions serve as the basis for quantitative methods for determining mercury, tin, zinc and cadmium.<sup>3</sup>

**Determination of mercury.** Mercury is quantitatively precipitated by adding tetraphenylarsonium chloride to a solution containing mercuric chloride and sodium chloride. Mercury can be determined indirectly by precipitating with a measured excess of a standardized solution of the reagent, and then titrating the excess iodometrically.<sup>4</sup> The reaction upon which the standardization of a solution of the reagent depends is given by the following equation:

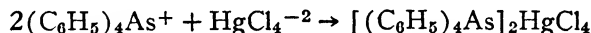


The titration should take place in about 100 ml. of a neutral or slightly acid solution which is saturated with sodium chloride just before the end-point is reached, and the end-point is then determined potentiometrically with a smooth platinum electrode against a calomel cell.<sup>3</sup>

**Reagent.** Dissolve 5-10 g. of tetraphenylarsonium chloride in a liter of distilled water and standardize potentiometrically with a standard iodine solution.

**Procedure.** Dilute the solution containing 0.5-100 mg. of mercury to 30 ml. and add sodium chloride to form a 1.0-2.5 M solution after the addition of the reagent. Then add an excess of the standardized 0.01-0.02 M reagent with constant stirring. Not more than 10 ml. of the reagent in excess should be used. The volume of the solution should now be 60-120 ml., depending upon the quantity of mercury present. Allow the mixture to stand for 15-60 minutes and filter through a Gooch crucible. Wash the precipitate several times with a saturated solution of sodium chloride, and then titrate the filtrate and washings potentiometrically with standardized 0.01-0.03 N iodine solution. The volume of tetraphenylarsonium chloride solution used to precipitate the mercury is obtained by difference.

The calculation is based on the following equation:



1 ml. 0.01 M reagent = 1.0031 mg. of mercury

The error obtained with 0.5-107 mg. of mercury is approximately  $\pm 0.06$  mg.

The precipitation of mercury may be carried out in a solution which is 1 N in any acid except nitric acid. The precipitate does not form in an alkaline solution. Permanganate, perrhenate, perchlorate, periodate, iodide, bromide, fluoride, tungstate, chromate, thiocyanate, bismuth, platinum, tin, zinc, cadmium and tetravalent titanium interfere. Interference due to copper, tin, manganese, iron and titanium can be prevented by converting into suitable stable complex ions. The effect of various reagents in eliminating interference by various metals in the determination of mercury by tetraphenylarsonium chloride is given in Table 50.

**Determination of tin.** Tin is determined by a method similar to that used for mercury. Tin is precipitated quantitatively as  $[(\text{C}_6\text{H}_5)_4\text{As}]_2\text{SnCl}_6$  with a measured excess of standardized tetraphenylarsonium chloride solution, and the excess is then determined by titration with iodine. It is possible to dissolve the tin precipitate in hot water and titrate the solution directly.<sup>4</sup>

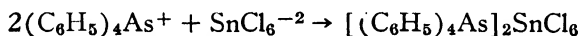
**Procedure.** To a solution containing 0.8-84 mg. of tin, dissolved in the smallest possible volume of water, add 2 ml. of concentrated hydrochloric acid and sufficient sodium chloride to make the solution 2.5-3.0 M in a final volume of 60 ml. Then add a measured volume of standardized 0.01-0.02 M tetraphenylarsonium chloride solution, known to be in excess, and add with stirring sufficient water to make the total volume 60 ml. The acid concentration should be 0.4-1.0

TABLE 50.—ELIMINATION OF INTERFERENCE IN THE DETERMINATION OF MERCURY  
(Volume = 60 ml.; mercury present = 25.64 mg.; conc. of sodium chloride = 1.1-2.3 M)

Ion Present	mg.	Added Reagent	Mercury Found mg.	Mercury Error mg.
Cu <sup>2+</sup>	400	3 g. sodium citrate and citric acid to acidify	25.67	+0.03
Mn <sup>2+</sup>	1200	4.7 g. of potassium tartrate	25.74	+0.10
Sn <sup>4+</sup>	32	Potassium tartrate and tartaric acid	25.65	+0.01
Ti <sup>4+</sup>	90	Sodium oxalate and HCl	25.69	+0.05
Fe <sup>3+</sup>	21	2 g. Na <sub>2</sub> HPO <sub>4</sub> and 2 ml. H <sub>3</sub> PO <sub>4</sub>	25.67	+0.03
Fe <sup>3+</sup>	103	2 g. Na <sub>2</sub> HPO <sub>4</sub> and 2 ml. H <sub>3</sub> PO <sub>4</sub>	25.64	.0
Fe <sup>3+</sup>	206	2 g. Na <sub>2</sub> HPO <sub>4</sub> and 2 ml. H <sub>3</sub> PO <sub>4</sub>	25.69	+0.05
Fe <sup>3+</sup>	309	3 g. Na <sub>2</sub> HPO <sub>4</sub> and 2 ml. H <sub>3</sub> PO <sub>4</sub>	25.69	+0.05
Fe <sup>3+</sup>	515	3 g. Na <sub>2</sub> HPO <sub>4</sub> and 2 ml. H <sub>3</sub> PO <sub>4</sub>	Unsatisfactory	Unsatisfactory

M. Allow the precipitate to settle for 30-60 minutes and filter through a Gooch crucible. Wash the precipitate several times with a saturated sodium chloride solution, and titrate the filtrate and washings with 0.02-0.03 N iodine solution. The volume of tetraphenylarsonium chloride solution required to precipitate tin is determined by difference.

The calculation is based upon the following equation:



One ml. 0.01 M reagent = 0.5935 mg. of tin.

Ferric iron, more than 25 mg. of ferrous iron, platinum, gold, bismuth, mercuric, mercury, cadmium, zinc, thallium, antimony, trivalent arsenic, uranium, fluoride, oxalate, phosphate, acetate, citrate, alkaline substances and all anions precipitated by tetraphenylarsonium chloride must be absent.

**Determination of cadmium and zinc.** In highly concentrated chloride solutions containing cadmium and zinc salts, the complex chloride ions of cadmium and zinc,  $\text{CdCl}_4^{-2}$  and  $\text{ZnCl}_4^{-2}$  form insoluble white precipitates with tetraphenylarsonium chloride. These precipitates have the composition:  $[(\text{C}_6\text{H}_5)_4\text{As}]_2\text{CdCl}_4$  and  $[(\text{C}_6\text{H}_5)_4\text{As}]_2\text{ZnCl}_4$ . These compounds are quantitatively precipitated in solutions containing a suitable quantity of sodium chloride, but they are soluble in water. Because of this relatively high solubility of the zinc and cadmium compounds, the determination of these substances by methods similar to those described for mercury and tin are subject to more interference.

A 0.015-0.02 M solution of tetraphenylarsonium chloride should be used for the precipitation, and the titration of the excess reagent should be made with a 0.02-0.025 N iodine solution containing 6-10 g. of potassium iodide per liter. The sodium chloride concentration should range from 2.5-3.5 M. The high sodium chloride concentration makes necessary a limited excess of tetraphenylarsonium chloride, since this compound is only slightly soluble in concentrated sodium chloride solutions. The calculations are based on the following relationships: 1 ml. 0.01 M tetraphenylarsonium chloride solution = 0.5621 mg. cadmium; 1 ml. 0.01 M reagent = 0.3269 mg. zinc.<sup>4</sup>

**Determination of rhenium.** Tetraphenylarsonium chloride reacts with soluble perrhenates to form a white crystalline precipitate of  $[(\text{C}_6\text{H}_5)_4\text{As}]\text{ReO}_4$ . This precipitate can be dried and weighed, or the precipitate may be formed by using a measured excess of standardized tetraphenylarsonium chloride solution, and determining the excess potentiometrically by titration with iodine.<sup>5</sup>

**Procedure.** To a solution containing 0.4-1.33 mg. of perrhenate ion, add sufficient sodium chloride to make the final concentration 0.5 M, and then add a measured excess of tetraphenylarsonium chloride. The total volume should be about 25-60 ml. Stir well and allow to stand for several hours or preferably overnight. Filter through a Gooch crucible, wash several times with ice water, and dry at 110° C. Weigh as  $[(\text{C}_6\text{H}_5)_4\text{As}]\text{ReO}_4$ . To obtain the weight of perrhenate, multiply the weight of the precipitate by 0.3952.

Accurate results are obtained by this method in solutions ranging from strongly ammoniacal to fairly strongly acidic. Permanganate, perchlorate, per-



iodate, iodide, bromide, fluoride, thiocyanate, mercury, tin, bismuth and vanadyl ions interfere. Very little nitric acid is permissible, but the effect of molybdate can be overcome by the addition of ammonia or tartaric acid.

1. F. F. Blicke and C. Marzano, *J. Am. Chem. Soc.* **55**, 3056 (1933).
2. F. F. Blicke and E. Monroe, *J. Am. Chem. Soc.* **57**, 720-22 (1935).
3. H. H. Willard and G. M. Smith, *Ind. Eng. Chem., Anal. Ed.* **11**, 186-8 (1939); *C.A.* **33**, 4154 (1939).
4. H. H. Willard and G. M. Smith, *Ind. Eng. Chem., Anal. Ed.* **11**, 269-74 (1939); *C.A.* **33**, 4899 (1939).
5. H. H. Willard and G. M. Smith, *Ind. Eng. Chem., Anal. Ed.* **11**, 305-6 (1939); *C.A.* **33**, 5315 (1939).

## TRIPHENYLTIN CHLORIDE

$C_{18}H_{15}SnCl$

Mol. Wt. 385.46

$(C_6H_5)_3SnCl$

**Use:** Detection and determination of fluoride.

Triphenyltin chloride is a colorless, crystalline solid. It melts at 106° C. It is readily soluble in most common solvents.

**Preparation.** *Tetraphenyltin.* Mix 60 g. of bromobenzene with absolute ether, and add 9 g. of magnesium metal. When the magnesium has dissolved, add dropwise at ordinary temperature 15 g. of stannic chloride and heat the mixture for 2 hours under reflux. Decompose the mass with water and acidify with dilute hydrochloric acid. Filter off the white solid and dry on a porous plate. Purify by crystallizing from pyridine.<sup>1</sup>

*Triphenyltin chloride:* Place 15 g. of tetraphenyltin in a distilling flask equipped with a reflux condenser and having a side arm closed by a stopper. Add 97.5 g. of chloroform. Heat the mixture to boiling, and add, while boiling, 9 g. of iodine in small portions. At first the color is immediately discharged after the addition of the iodine, but toward the end a brown color remains after boiling for one hour. Distill off the chloroform on a water-bath, and remove the iodobenzene by distilling the mixture at a pressure of 13 mm. Dissolve the residue in ether and filter to remove any unchanged tetraphenyltin. Shake the ether solution in a separatory funnel with 3 portions of 30 per cent sodium hydroxide solution and separate. The ether layer contains triphenyltin hydroxide. Wash thoroughly the ether layer, and any of the hydroxide which may separate, with cold water by shaking in a separatory funnel. Then shake the ether solution with concentrated hydrochloric acid to convert the hydroxide to triphenyltin chloride. Separate the layers and dry the ether layer over anhydrous sodium sulfate. Evaporate the liquid until crystals begin to separate. Recover the product by filtration and recrystallize from ether. Dry in air at room temperature.<sup>2</sup>

**Detection and determination of fluorine.** Krause and Becker<sup>3</sup> first prepared triphenyltin fluoride and noted that it was very insoluble in cold water.

The solubility of the fluoride in alcohol is 0.05 g. per liter. The precipitation cannot be carried out in water, since triphenyltin chloride is insoluble in water and will precipitate. The determination is best carried out in 60-70 per cent alcohol by volume. Allen and Furman<sup>4</sup> have based a procedure for the determination of fluorine upon the insolubility of triphenyltin fluoride.

**Reagent.** Add 20 g. of triphenyltin chloride to 1 liter of 95 per cent alcohol and shake vigorously. Filter and use the clear filtrate as the reagent.

**Procedure.** Add 95 per cent ethyl alcohol to an aqueous solution of the fluoride so that the final concentration of the alcohol is about 60-70 per cent by volume. Heat to boiling. Dilute about 2 times the calculated quantity of the reagent solution, containing 0.02 g. per ml. with an equal volume of 95 per cent alcohol, and heat to boiling. Then add this solution slowly to the hot fluoride solution with rapid stirring, and again heat the mixture to boiling. Remove from the source of heat and allow the mixture to cool while stirring. Allow to stand overnight, and pack in ice and allow to stand for 1 hour. Filter through a sintered glass crucible, and wash with 95 per cent alcohol saturated with triphenyltin fluoride. Use 50 ml. of this solution at room temperature. Dry the precipitate for 30 minutes at 110° C., cool in a desiccator, and weigh as  $(C_6H_5)_3SnF$ . The factor for fluorine is 0.05153.

The solution to be precipitated should have a pH of 7-9. If the solution is acid, some of the fluoride may be lost on boiling, and if too basic some triphenyltin may be precipitated.

Many inorganic salts are insoluble in 60-70 per cent alcohol and may precipitate if present in high concentration.

The results obtained in determining fluorine in fluorspar by precipitating with triphenyltin chloride are given in Table 51.

TABLE 51.—DETERMINATION OF FLUORINE IN FLUORSPAR  
WITH TRIPHENYLTIN CHLORIDE

Determination	Weight of Precipitate mg.	Weight of Fluorine Found mg.	Weight of Fluorine Calculated mg.	Average Error mg.
1-4	89.8-89.0	4.63-4.59	4.51	0.10
5-8	113.5-110.8	5.85-5.71	5.75	0.06
9-12	134.1-131.7	6.91-6.79	6.79	0.08

1. P. Pfeiffer and K. Schnurmann, *Ber.* **37**, 319 (1904).
2. R. F. Chambers and P. C. Scherer, *J. Am. Chem. Soc.* **48**, 1055 (1926).
3. E. Krause and R. Becker, *Ber.* **53**, 183 (1920).
4. N. Allen and N. H. Furman, *J. Am. Chem. Soc.* **54**, 4625-31 (1932); *C.A.* **27**, 681 (1933).

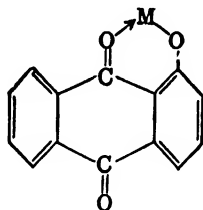
## CHAPTER XIV

### LAKE-FORMING DYESTUFFS

The lake-forming dyes are hydroxy-substitution products of aromatic compounds, but since they are commercial dyes, they are grouped together in the section on dyes rather than with the phenols. These compounds form intensely colored, insoluble lakes with such metals as aluminum, chromium, ferric iron, magnesium and cadmium.

Some insight into the problem of lake formation has been provided by a study of the structure of mordant dyes. Werner<sup>1</sup> has pointed out that the action of mordants is due to the formation of coordinated ring compounds with the metal atom. Werner showed that many mordant dyes not only possess structures similar to those of compounds known to form such rings, but demonstrated also that cloth mordanted with chromium or iron salts is actually dyed when treated with a solution of a  $\beta$ -diketone or a  $\beta$ -ketonic ester, such as acetylacetone or acetoacetic ester. These compounds alone are colorless, and the color formed in the dyeing process can be interpreted as due to the formation of colored chelate compounds with the iron or chromium salt.

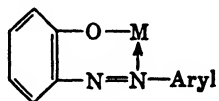
A great many of the commercial dyes of established constitution can be mordanted with salts of the polyvalent metals. With the exception of a limited few of these, all have a replaceable hydrogen atom and a coordinating group so located as to permit the formation of a 5- or 6-membered ring, which is connected to an aromatic ring in the ortho-position. Most of these rings are of types known from other evidence to occur in chelate compounds. For example, the most important type of chelate ring is the 6-membered ring containing two conjugated double bonds. Numerous compounds capable of forming rings of this type are found among the mordant dyes. Since all alizarin dyes are substitution products of 1-hydroxyanthraquinone, all compounds of this class can form the ring structure



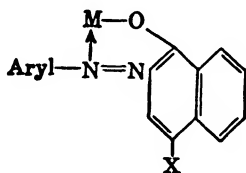
in which  $M$  is one equivalent of the metal of the mordant.

Among the azo dyes, two classes are always mordant dyes: (1) those in which that part of the molecule which is derived from the diazotized amine has an hydroxyl group in the ortho-position; and (2) those in which the com-

pound used as the coupling agent is a derivative of salicylic acid. Compounds of the first class form structures of the type

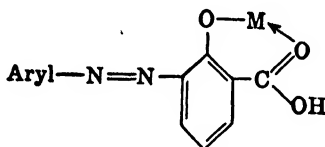


The same ultimate ring structure is formed if the coupling agent has an ortho-hydroxyl group instead of the diazotized amine. For example, by coupling a simple diazotized amine with  $\beta$ -naphthol, or a para-substituted  $\alpha$ -naphthol, structures of the type



are formed. When the azo group does not couple in the ortho-position to the hydroxyl group, the compound formed is not a mordant dye.

The type of compound formed from dyes of the second class is shown by the following formula



While it has been definitely established that chelation undoubtedly plays a part in mordant dyeing, the problem of lake constitution does not appear to have been definitely solved. Since the analytical reactions employing lake-forming dyes usually depends on the precipitation of the slightly soluble metal hydroxide in the presence of the dye, color lakes are often thought to be due to the adsorption of the dye on the hydrous oxides, and it is difficult to determine whether they are adsorption complexes or chelate salts.<sup>2</sup> According to Yoe,<sup>3</sup> however, since lake-forming dyes possess structures capable of chemical combination, it appears likely that chelate salts are actually formed; and this seems the more probable, since it has not been definitely proved otherwise.

Additional information on the character of lake-forming dyes is contained in the chapter on the anthraquinone dyes.

Included also in the section on lake-forming dyes are several dyes which are not phenolic compounds, but which behave similarly by forming colored adsorption products. Among these are the aminoazo compounds which have proved so useful for the detection of cadmium.

1. A. Werner, *Ber.* **41**, 1062 (1908).
2. H. B. Weiser and E. F. Porter, *J. Phys. Chem.* **31**, 1383, 1704, 1824 (1927).
3. J. H. Yoe and L. A. Sarver, *Organic Analytical Reagents*, p. 131, John Wiley, New York (1941).

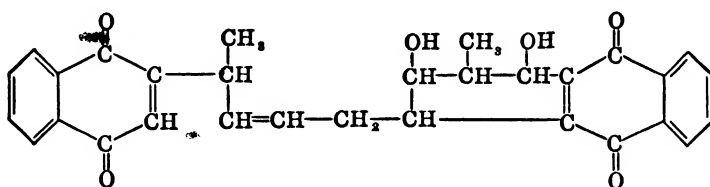
**ALKANNIN**

Synonym: Alkanet extract, anchusin, alcannin

**Use:** Detection of aluminum, beryllium, cobalt, iron, magnesium, nickel, silicon, uranium, and zinc.

Alkannin is a coloring matter of somewhat uncertain composition obtained from Alkanet root. It was for some time regarded as a derivative of anthraquinone, but now it has been rather definitely established as a derivative of naphthazarin. According to the work of Raudnitz and co-workers,<sup>1</sup> Dieterle and coworkers,<sup>2</sup> and Betrabet and Chakravarti<sup>3</sup> the following probable structure has been assigned:

Color Index: 1240



The dye is obtained as a dark red, amorphous, slightly acid powder. It is slightly soluble in water, soluble in alcohol, benzene, chloroform, ether, and oils, and also in alkalies with the formation of blue solutions.

**Detection of magnesium.** As early as 1880 Lepel<sup>4</sup> reported the use of a solution of alkanet red for the detection of magnesium. A solution prepared by dissolving the coloring matter in a mixture of 2 parts ethyl alcohol and one part ether, and then diluting with water, gives an absorption band composed of three separate bands. The violet-colored solution produced by the addition of ammonium carbonate to this mixture is changed to blue by the presence of a very small quantity of magnesium salt, and a characteristic fourth absorption band appears. In this way 0.05 mg. of magnesium in 1 ml. of solution can be detected.

Eisenlohr<sup>5</sup> has studied the reactions of alkannin with solutions of magnesium, barium, calcium, strontium, and manganese salts. His procedure is as follows:

**Procedure.** Add one drop 2 N ammonium carbonate solution to 5 ml. of the colored solution of alkannin in 96 per cent alcohol. No change in color occurs, but with the addition of one drop of a neutral solution of magnesium, barium, calcium, strontium, or manganese salt, the following colors are observed:

Magnesium	.....	blue-violet
Barium	.....	unchanged
Calcium	.....	blue
Strontium	.....	blue-violet
Manganese	.....	blue-violet

Magnesium, strontium, and manganese are not distinguishable, but if the solutions are acidified with one drop (or not more than 2 drops) of 2 N hydro-

chloric acid (bright red precipitate) and are then treated with the same number of drops of 2 N ammonium carbonate, the blue-violet color returns if magnesium is present.

It is important to use an alcoholic solution of the dye, undiluted with water, since otherwise ammonium carbonate is hydrolyzed, and the resulting ammonia gives a blue coloration in all cases.

If the test for magnesium is carried out in a cold solution made alkaline with sodium hydroxide, 0.5-1.0 mg. of magnesium is required for a positive reaction; but if a little ethylenediamine is substituted for the sodium hydroxide and slight heat is applied, the reaction becomes 1000 times as sensitive.<sup>6</sup> As reagent, use a 0.05 per cent alcoholic solution of alkannin, and just before using add a few drops of 10 per cent ethylenediamine solution. Then shake and warm.

**Detection of aluminum.** Estill and Nugent<sup>7</sup> use alkanet root tincture as a confirmatory test for aluminum.

**Procedure.** Dissolve the precipitate suspected of being aluminum hydroxide in 6 N sulfuric acid, dilute with a little water, and add sufficient tincture of alkanet root to color the solution a ruby-red. Then add 6 N ammonium hydroxide until the red color changes to blue, and add 5 ml. in excess. Within 5 minutes a purple lake rises to the surface if aluminum is present.

This method may be made semi-quantitative by measuring the volume of the lake formed. Its volume in milliliters is approximately equal to the number of milligrams of aluminum present.

Silicic acid and tetravalent titanium give blue-gray precipitates, and stannic tin causes a red-brown precipitate. Chromium, iron, stannous tin, mercury, bismuth, and lead cause no confusion.

According to Dubsky and Wagner,<sup>8</sup> the above test fails in an ammoniacal solution with less than 0.05 mg. of aluminum. Gotō<sup>8</sup> reports that 10 $\gamma$  of aluminum can be detected by a fluorescence method.

**Detection of beryllium.** Dubsky and Krametz<sup>9</sup> propose the following test for beryllium:

**Reagent.** Dissolve 0.05 g. of alkannin in 100 ml. of ethyl alcohol.

**Procedure.** When ready to use, mix 30 drops of the above solution with 5 drops of 10 per cent ethylenediamine solution. This gives a dirty blue reagent. On dilution with water this solution becomes a clear blue, but the addition of a solution containing beryllium causes the color to change to a red-violet. In this way as little as 1.2 $\gamma$  of beryllium can be detected.

The above test is somewhat less delicate if ammonium hydroxide is used in place of ethylenediamine.

As little as 0.5 $\gamma$  of beryllium can be detected by means of a fluorescent method.<sup>10</sup>

**Reactions of cations.** Formanek<sup>11,12</sup> has studied the reactions of a number of other cations with tincture of alkannin. His results are as follows:

(a) *Nickel*: Nickel in a neutral solution gives a violet color, and in an ammoniacal solution a blue color. This test is sensitive to 150 $\gamma$  of nickel in 5 ml. of solution.

(b) *Cobalt*: A neutral solution of cobalt gives a violet color with tincture of alkannin. The test will detect 250 $\gamma$  of cobalt in 5 ml. of solution.

(c) *Iron*: A neutral solution of a ferrous salt gives a blue-violet color with alkannin. A red-brown color is obtained in an ammoniacal solution. A gray-blue color is obtained with a neutral solution of a ferric salt. In an ammoniacal solution, a gray precipitate forms. The sensitivity of the ferric iron reaction is 500 $\gamma$  in 5 ml.

(d) *Uranium*: A neutral solution of a uranium salt gives a green color with alkannin. In the presence of ammonia, a green precipitate forms. The sensitivity of the reaction is 1000 $\gamma$  in 5 ml.

(e) *Zinc*: An ammoniacal solution of zinc forms a violet color with alkannin, but the test is not sensitive.

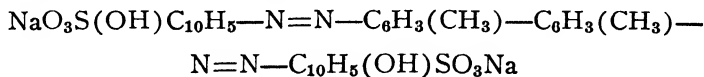
1. H. Raudnitz, and co-workers, *Ber.* **64B**, 1835-41 (1931); *C.A.* **25**, 5418 (1931); *Ber.* **65B**, 159-60 (1932); *C.A.* **26**, 2453 (1932).
2. H. Dieterle, and co-workers, *Ber.* **64B**, 2086-90 (1931); *C.A.* **26**, 134 (1932).
3. M. V. Betrahbet and G. C. Shakravarti, *J. Indian Inst. Sci.* **16A**, 41-51, 52-3 (1933); *C.A.* **28**, 1038 (1934).
4. F. v. Lepel, *Ber.* **13**, 763 (1880).
5. F. Eisenlohr, *Ber.* **53**, 1476-7 (1920); *C.A.* **15**, 218 (1921).
6. J. V. Dubsky and E. Wagner, *Mikrochemie.* **17**, 186-90 (1935); *C.A.* **29**, 5375 (1935).
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9. J. V. Dubsky and E. Krametz, *Mikrochemie.* **20**, 57-8 (1936); *C.A.* **30**, 5143 (1936).
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## AZO BLUE

$C_{34}H_{24}O_8N_4S_2Na_2$

Mol. Wt. 726.65

Color Index: 463



**Use:** Detection of magnesium.

The dye occurs as a bluish-black powder which possesses a metallic luster. It dissolves in water with a violet solution, in sodium hydroxide with a magenta-red solution, and in sulfuric acid with a blue solution.

**Preparation.** Stir 50 g. of tolidine with 1 liter of water and 60 g. of hydrochloric acid ( $d = 1.16$ ) and tetrazotize with a solution of 22 g. of sodium

nitrite and ice. Add the mixture slowly to a solution of 85 g. of 1-naphthol-4-sulfonic acid (sodium salt) and 40 g. sodium carbonate in 2 liters of water. Salt out the dye.

**Detection of magnesium.** The dye azo blue has been used by Broda<sup>1</sup> as a satisfactory reagent for the detection of magnesium in plant materials. It is particularly useful to show the distribution of magnesium where the existence of magnesium compounds is already known, and is also useful in certain doubtful cases for the identification of crystals of  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ . This dye, however, should be used only as a supplementary reagent, since it is non-specific for magnesium. Eegriwe<sup>2,3</sup> has also used this dye as a general reagent for magnesium. The distribution of magnesium compounds in plant materials is demonstrated by staining a section with 1-2 drops of an aqueous 0.1 per cent solution of azo blue, mixed with an equal volume of 10 per cent sodium hydroxide solution. Magnesium is stained a purple color.

Magnesium can be detected in the absence of cobalt, nickel, and chromium by adding 1-2 drops of an 0.01 per cent aqueous solution of the dye to 1 drop of the solution to be tested, followed by an excess of 2 N sodium hydroxide. An alkaline solution of the dye is pink in color, but this changes to violet in the presence of magnesium. With 5 ml. of solution, 1 $\gamma$  of magnesium can be detected. The limiting concentration is 1:5,000,000.

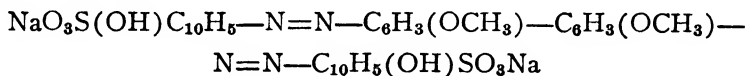
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2. E. Eegriwe, *Z. anal. Chem.* **76**, 354-9 (1929); *C.A.* **23**, 2903 (1929).
3. Z. Karaoglanov, *Z. anal. Chem.* **119**, 16-55 (1940).
4. J. V. Dubsky and A. Okac, *Chem. Listy*, **24**, 492 (1930); *C.A.* **25**, 2660 (1931).
5. K. Heller, *Mikrochemie*, **9**, 451 (1931).

## BENZOAZURINE G

$\text{C}_{34}\text{H}_{24}\text{O}_{10}\text{N}_4\text{S}_2\text{Na}_2$

Mol. Wt. 758.66

Color Index: 502



**Use:** Detection of magnesium.

Benzoazurine G is a bluish-black powder with a bronze luster. It dissolves in water with a bluish-violet solution, and in aqueous sodium hydroxide with a magenta-red solution. It also dissolves in sulfuric acid with a blue color.

**Preparation:** Dissolve 3 g. of sodium nitrite in water and add to a solution of 5 g. of dianisidine in 10 g. of hydrochloric acid ( $d = 1.16$ ) and 75 ml. of water cooled with ice. Add the resulting mixture to 11 g. of 1-naphthol-4-sulfonic acid (sodium salt) and 5 g. sodium carbonate in 200 ml. of water. When the reaction is complete, salt out.

**Detection of magnesium.** Benzoazurine G imparts to a precipitate of magnesium hydroxide a characteristic violet-blue coloration which is useful in identifying small quantities of magnesium.

To test for magnesium, proceed as follows:<sup>1</sup>



**Reagent.** Dissolve 0.1 g. of the dye in 100 ml. of water.

**Procedure.** First neutralize the solution to be tested to litmus, and use 1 drop of this solution for the test. Treat this drop with 1-2 drops of the reagent and 1 ml. of 25 per cent ammonium hydroxide. If magnesium is present a blue to violet-blue color or precipitate forms.

5γ of magnesium in 5 ml. of solution, or 2γ magnesium in 0.5 ml. yields a blue color. Greater quantities of magnesium yield a violet-blue color or precipitate. The concentration limit is 1:90,000. Anions which form insoluble precipitates with magnesium in neutral or ammoniacal solutions interfere. Copper, cobalt, and nickel in large quantities form complexes with ammonia, and must be absent while making the test.

Silver, mercury, tungstate, copper, bismuth, tin, antimony, arsenate, molybdate, beryllium, vanadyl, uranyl, manganese, chromium, aluminum, iron, lanthanum, titanium and ammonium ions interfere with the test, but lead, cadmium, zinc, nickel, calcium, strontium, barium, potassium and sodium may be present without appreciable effect.

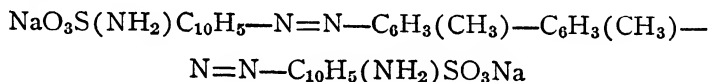
1. E. Eegriwe, *Z. anal. Chem.* **108**, 34-7 (1937); *C.A.* **31**, 2961 (1937).

### BENZOPURPURIN 4B (Gr-E)

$C_{34}H_{26}N_6O_6S_2Na_2$

Mol. Wt. 724.67

Color Index: 448



**Use:** Detection of aluminum, magnesium, mercury, silver and uranium.

The dye is a brown powder. It dissolves in water with the formation of a brown-red solution. It is also soluble in sodium hydroxide and sulfuric acid.

**Preparation:** Dissolve 18.4 g. of *o*-tolidine in 300 ml. of water and 20 ml. of concentrated hydrochloric acid. Use heat if necessary. Add ice until the temperature falls below 5° C. Add 30 ml. of concentrated hydrochloric acid, and about 14.4 g. of sodium nitrite in a 10 per cent aqueous solution until diazotization is complete. Dissolve 150 g. of sodium naphthionate in the least possible quantity of water, and to this slowly add the diazo solution with stirring. Allow the mixture to stand 30 minutes, and add gradually a solution of 35 g. of sodium carbonate so that during further stirring the solution remains alkaline. Heat the mixture slowly to about 80° C., and saturate with salt. Cool, filter the dye, wash with a saturated salt solution, and dry.

**Detection of magnesium.** Eegriwe<sup>1</sup> reports that benzopurpurin 4B may be used for the detection of magnesium, although Dubsy and Okac<sup>2</sup> claim that only a vague color change occurs with magnesium hydroxide.

**Procedure.** Add 1-2 drops of a 0.01 per cent aqueous solution of the dye to 1 drop of the solution to be tested, and make alkaline with an excess of

2 N sodium hydroxide. The alkaline solution of the dye is orange in color, but this changes to pink in the presence of as little as 0.01 mg. of magnesium.

Nickel, chromium, and cobalt interfere.

Larsen<sup>4</sup> has used benzopurpurin 4B for the detection of magnesium in printing inks.

**Detection of silver.** When a 0.2 per cent aqueous solution of benzopurpurin 4B is placed in contact with a drop of a solution containing silver ions, a brown ring forms about a red spot, which appears like the drop of the dye solution. This test is given with only 0.03 mg. of silver.<sup>3</sup>

**Detection of mercury.** With a 0.2 per cent aqueous solution of the dye, mercurous ions give a reddish-violet color. With mercuric ions a bluish-gray ring is formed. Tests are given with 0.04 mg. of mercurous and 0.015 mg. of mercuric ions.<sup>3</sup>

**Detection of uranium.** As little as 0.035 mg. of uranium may be detected by the light brown ring which uranyl ions give with benzopurpurin.<sup>3</sup>

**Detection of aluminum.** Only .005 mg. of aluminum may be detected by the reddish-brown spot which benzopurpurin forms with solutions of aluminum salts.<sup>3</sup>

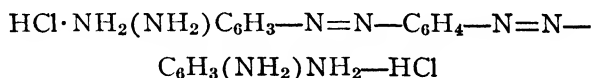
1. E. Eegriwe, *Z. anal. Chem.* **76**, 354-9 (1929); *C.A.* **23**, 2903 (1929).
2. J. V. Dubsky and A. Okac, *Chem. Listy* **24**, 492-3 (1930); *C.A.* **25**, 2660-1 (1931).
3. E. A. Kocsis, *Mikrochemie* **27**, 180-4 (1939); *C.A.* **34**, 51 (1940).
4. L. M. Larsen, *Ind. Eng. Chem., Anal. Ed.* **2**, 416 (1930); *C.A.* **24**, 6038 (1930).
5. K. Heller, *Mikrochemie* **9**, 451 (1931).

## BISMARK BROWN

$C_{18}H_{20}N_8Cl_2$

Mol. Wt. 419.26

Color Index: 331



**Use:** Detection of antimony.

The dye occurs as a blackish-brown powder. It dissolves in water and alcohol to form a brown solution.

**Preparation:** Dissolve 7 g. of sodium nitrite in 70 ml. of water, and add to a very dilute solution of *m*-phenylenediamine (obtained by reducing 25 g. of *m*-dinitrobenzene with iron and hydrochloric acid) containing 14.5 g. of *m*-phenylenediamine. Then add 37 g. of hydrochloric acid at 10-15° C. Salt out and purify by dissolving several times in water and salting out again.

**Detection of antimony.** Bismark brown may be used as a fairly sensitive reagent for antimony.<sup>1</sup>

**Procedure.** To 5 ml. of a hydrochloric acid solution of an antimony salt, add a few drops of an aqueous solution of the dye, and then precipitate

with 5 N ammonium hydroxide. A flesh-colored precipitate forms if the concentration of the antimony ion is 10 mg. per ml. This test does not appear to be very sensitive.

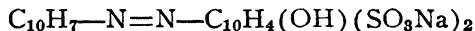
1. J. W. Smith and H. E. Rogers, *J. Chem. Ed.* **16**, 143-4 (1939) ; *C.A.* **33**, 3287 (1939).

### BORDEAUX RED

$C_{20}H_{12}N_2O_7S_2Na_2$

Mol. Wt. 502.42

Color Index: 88



**Use:** Detection of antimony and mercury.

The dye is a brown powder, which dissolves in water to form a magenta-red solution. It is moderately soluble in alcohol with which it forms a bluish-red solution. It dissolves in sodium hydroxide with a yellowish-brown color and in sulfuric acid with a blue color.

**Preparation:** Add 143 g. of  $\alpha$ -naphthylamine and 1 molecular proportion of hydrochloric acid to 4170 ml. of water, add ice until the temperature falls to 8° C., and then add 2 molecular proportions of hydrochloric acid. Remove a small sample and add a little sodium nitrite. If a clear brown solution is formed, proceed with the diazotization, but if a precipitate forms, add more acid until a diazotized solution remains clear. Now add quickly a concentrated solution of 72 g. of sodium nitrite at 8° C.

Add the diazo solution to a cold solution of 355 g. of R-salt dissolved in 115 g. of sodium hydroxide and 4170 ml. of water. The R-salt and alkali must be present in excess. Allow the mixture to stand, heat to 80° C., salt out, and filter.

**Detection of antimony.** Antimony may be detected in the presence of stannous tin by the following procedure.<sup>1</sup>

**Procedure.** To 5 ml. of a hydrochloric acid solution of antimony salt, add a few drops of an aqueous solution of the dye, and then precipitate with 5 N ammonium hydroxide. With antimony a light pink precipitate and a pink solution are obtained. With tin a white precipitate and a colorless solution are formed.

The test may be obtained with as little as 1 mg. of antimony per ml. of solution. If the amount of tin present is not greater than the amount of antimony, the pink-colored solution is observed indicating antimony.

**Detection of mercury.** Mercury is detected as follows:<sup>1</sup>

**Procedure.** To 5 ml. of solution containing 10 mg. of mercurous ion per ml., add a few drops of an aqueous solution of the dye and precipitate with 4 N sodium carbonate. A dark green precipitate forms with mercurous mercury.

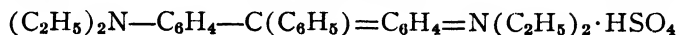
This reaction is not very sensitive.

1. J. W. Smith and H. E. Rogers, *J. Chem. Ed.*, **16**, 143-4 (1939) ; *C.A.* **33**, 3287 (1939).

**BRILLIANT GREEN** $C_{27}H_{33}N_2 \cdot SO_4H$ 

Mol. Wt. 482.60

Color Index, 662.

**Use:** Detection of barium, mercury, and thallium.

The dye occurs as small, glistening, golden crystals. These are soluble in water and alcohol with the formation of green solutions. The sulfuric acid solution of the dye is yellow.

**Preparation:** Mix 60 g. of diethylaniline and 22 g. of benzaldehyde, and add 32 g. of anhydrous oxalic acid with stirring. From this point, proceed as in the preparation of malachite green (page 515).<sup>1,2</sup>

**Detection of mercury and barium.** A dark green precipitate forms when mercurous mercury is precipitated with sodium carbonate in the presence of brilliant green:<sup>3</sup>

**Procedure.** To 5 ml. of a solution of a mercurous salt, containing 10 mg. per ml. of mercury, add a few drops of an aqueous solution of the dye, and then precipitate with 4 N sodium carbonate. A dark green precipitate forms with mercurous mercury.

Barium may be detected by a procedure similar to that used for mercury. A pink precipitate forms with barium.<sup>3</sup>

**Detection of tantalum.** As little as 0.4% of tantalum can be detected by the coarse, flaky, dark green precipitate with a 0.25 per cent aqueous solution of brilliant green. Tungsten, molybdenum, titanium, and tin interfere.<sup>4</sup>

1. O. Doebner, *Ber.* **13**, 2229 (1880).
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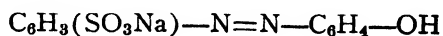
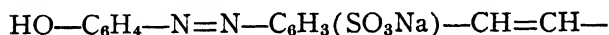
**BRILLIANT YELLOW**

Synonym: Sodium salt of 2,2'-disulfostilbene-4,4'-disazobisphenol

 $C_{26}H_{18}O_8N_4S_2Na_2$ 

Mol. Wt. 624.52

Color Index, 364.

**Use:** Detection of cobalt, magnesium and nickel.

Brilliant yellow is a light brown powder which dissolves in water with a red-dish-yellow solution.

**Preparation:** Tetrazotize an aqueous solution containing 20 g. of the sodium salt of diaminostilbenedisulfonic acid with 7 g. of sodium nitrite and

25 g. of hydrochloric acid. Allow the mixture to stand for a short time, and then add an alkaline solution containing a little more than the theoretical quantity of phenol.

**Detection of magnesium, cobalt and nickel:** Brilliant yellow may be used in a reaction for the detection of magnesium, which is based upon the color change which occurs when magnesium hydroxide is precipitated in the presence of the dye. A rose-red color is obtained with magnesium. Cobalt and nickel may be detected in a similar manner. A 1 per cent aqueous solution of the dye is used as the reagent. The reaction is capable of detecting 4 mg. of magnesium per liter and 2 mg. of cobalt or nickel per liter.<sup>1,2,3</sup>

1. I. M. Kolthoff, *Z. anal. Chem.* **87**, 43 (1932).
2. I. M. Kolthoff, *Mikrochemie Emich Festschr.* 186 (1930).
3. Z. Karaoglanov, *Z. anal. Chem.* **119**, 16-55 (1940).

### BRILLIANT VIOLET

$C_{31}H_{34}N_3Cl$

Mol. Wt. 484.04

Color Index, 683.



**Use:** Detection of mercury, silver and tin.

This dye is usually obtained as lumps or as a powder possessing a bronze luster. It dissolves in water and alcohol with blue-violet solutions. It also dissolves in sulfuric acid to form a yellow solution.

**Preparation:** Mix 6 g. methyl violet, 6 g. alcohol, and 3 g. of benzyl chloride and sufficient sodium carbonate to keep the mixture alkaline, and then heat to 80° C. for 6-8 hours under reflux. Neutralize with hydrochloric acid, boil with water, and filter. Finally, precipitate the dye from the filtrate with salt.<sup>2,3</sup>

**Detection of silver, mercury, and tin.** Brilliant violet may be used as a fairly satisfactory reagent for silver, mercury and tin.<sup>1</sup>

**Procedure.** To 5 ml. of solution containing 10 mg. of silver ion per ml., add a few drops of an aqueous solution of the dye, and then precipitate with 4 N sodium carbonate. A green precipitate forms with silver.

Mercurous salts may be detected by a similar method:<sup>1</sup> A yellow-brown precipitate forms with mercurous mercury.

Tin is detected as follows:<sup>1</sup>

**Procedure.** To 5 ml. of an hydrochloric acid solution of stannous tin, add a few drops of an aqueous solution of the dye, and then precipitate with 5 N ammonium hydroxide. A pale blue precipitate forms with stannous ions.

1. J. W. Smith and H. E. Rogers, *J. Chem. Ed.* **16**, 143-4 (1939); *C.A.* **33**, 3287 (1939).
2. Ch. Lauth and E. Grimaux, *Bull. soc. chim.* **7**, 105 (1867).
3. O. Fischer and G. Körner, *Ber.* **16**, 2910 (1883).

***p*-NITRODIAZOAMINOAZOBENZENE**

Synonym: Cadion

 $C_{18}H_{14}O_2N_6$ 

Mol. Wt. 346.29

**Use:** Detection of cadmium and magnesium.

*p*-Nitrodiazoaminoazobenzene (cadion) is a yellow to orange solid. It darkens on heating at 192° C., and melts with partial decomposition at 197° C. At higher temperatures it decomposes completely with explosion. It is somewhat more soluble in benzene or acetone than in alcohol. It dissolves readily in alcoholic alkali with the formation of a beautiful purple color. It decomposes when treated with mineral acids.

**Preparation:** Dissolve 1.38 g. of *p*-nitroaniline in 20 ml. of approximately 5 N hydrochloric acid by heating to 70-80° C. Cool somewhat, and then pour with stirring on to about 25 g. of finely crushed ice in a beaker standing in ice water. Dissolve 0.69 g. of sodium nitrite in 10 ml. of water and add, all at once, with stirring, to the above ice-cold solution. After about 5 minutes, when diazotization is complete and all the *p*-nitroaniline is in solution without separation of any *p,p'*-diazaminobenzene, neutralize the solution with 3 N sodium carbonate solution (about 30 ml.), stir in 20 g. of sodium acetate, and filter the solution if necessary. Add the above solution with stirring to an ice-cold solution containing 1.97 g. of *p*-aminoazobenzene dissolved in a mixture of 50 ml. acetone with 150 ml. of alcohol. A voluminous yellow precipitate forms immediately. Allow the mixture to stand for 5 minutes and pour into 500 ml. of ice water. Filter through a Buchner funnel, wash with water, and finally with a 50 per cent alcohol-water mixture. Recrystallize from 600 ml. of boiling alcohol containing 2 drops of concentrated ammonium hydroxide. An orange precipitate is formed.<sup>1</sup>

**Detection of magnesium.** Dwyer<sup>1,2,6</sup> has studied the use of a number of nitrodiazoaminoazo dyes as sensitive reagents for the detection and estimation of magnesium, and has found that certain of these dyes give remarkably sensitive and highly selective adsorption colors with magnesium oxide and magnesium hydroxide. These range from violets to blues and greens. One of the most satisfactory of these dyes is *p*-nitrodiazoaminoazobenzene, which is usually designated by the shorter name of cadion. By means of this reagent as little as 0.1γ of magnesium can be detected in 1 ml. of solution. The following procedure is used for the magnesium test:

**Reagent.** The reagent is a 0.02 per cent solution of cadion in 100 ml. of alcohol to which 1 ml. of 2 N potassium hydroxide has been added.

**Procedure.** Add a few drops of the above reagent to a slightly acetic acid solution of the material to be analyzed, and then make alkaline with potassium hydroxide. A cornflower-blue precipitate or color appears if magnesium is present.<sup>6</sup> This reaction is sensitive to 0.1γ of magnesium per ml. in 5 ml. of solution.

This reaction is about five times as sensitive as that using the azoresorcinol derivative. Beryllium does not interfere.

Cadmium interferes with the magnesium test, since the dye is adsorbed by both magnesium and cadmium hydroxides giving a gradation in color which ranges from red to blue depending upon the relative quantities of cadmium and magnesium present. The test for cadmium with cadion can be prevented entirely by the addition of potassium cyanide just before making the mixture alkaline. Under these conditions the reagent gives a test only with magnesium.

**Detection of cadmium.** Dwyer<sup>1,3</sup> has used cadion for the detection of small quantities of cadmium:

**Reagent.** The reagent is a 0.02 per cent solution of the dye in alcohol which is 0.02 N in potassium hydroxide.

**Procedure.** Place a drop of the purple solution of the dye upon a strip of filter paper which rests upon thick blotting paper. Add a smaller drop of the solution to be tested, which has been made slightly acid with acetic acid. Finally add a large drop of 2 N potassium hydroxide solution. If cadmium is present, a bright pink center circle is obtained, and this is surrounded by a violet-blue ring. The test is sensitive to 1 drop of solution containing 0.5γ of cadmium per ml.

The reaction is particularly useful for detecting cadmium in the presence of considerable quantities of zinc. Silver, mercury, copper, nickel, iron, chromium, cobalt, magnesium and ammonium salts interfere, but the interference by all except silver, mercury and ammonium ions is eliminated by the addition of a little Rochelle salt. Silver is best removed by adding a crystal of potassium iodide, and mercury by precipitation as the sulfide.

Dobbins and Southern,<sup>4</sup> Miller,<sup>5</sup> and Davies<sup>7</sup> have used cadion for the detection of cadmium in a systematic scheme of analysis.

1. F. P. Dwyer, *Australian Chem. Inst. J. and Proc.* **4**, 26-34 (1937); *C.A.* **31**, 3412 (1937).
2. F. P. Dwyer, *Australian Chem. Inst. J. and Proc.* **3**, 184-6 (1936); *C.A.* **30**, 6302 (1936).
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4. J. T. Dobbins and J. A. Southern, *J. Chem. Ed.* **19**, 479-82 (1942); *C.A.* **37**, 47 (1943).
5. C. C. Miller, *J. Chem. Soc.* **144**, 786-92 (1941); *C.A.* **36**, 2225 (1942).
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7. W. C. Davies, *J. Chem. Ed.* **17**, 231-4 (1940); *C.A.* **34**, 4685 (1940).

**CADION 2β** Synonym: Nitronaphthalenediazoaminobenzene-4'-azobenzene



**Use:** Detection of cadmium and magnesium.

Cadion 2β consists of dark violet needles or a dark brown powder. It melts at 175° C. with decomposition. It dissolves readily by shaking with an alcoholic

solution of an alkali to yield a dark blue solution. The compound is destroyed by dilute mineral acids.

**Preparation:** Grind 0.47 g. of 4-nitro-1-aminonaphthalene in a mortar with 20 ml. of approximately 5 N hydrochloric acid and transfer the mixture to a beaker. Heat to 90° C. for about 2 minutes and then cool quickly in ice. In this way about 20 per cent of the amine dissolves while the remainder is in suspension as a very fine powder. To the ice-cold solution, add 0.2 g. of sodium nitrite dissolved in 1 ml. of water, and allow the mixture to stand at 0° C. for 1 hour with frequent stirring. Most of the amine dissolves to form a pale yellow solution. Add 30 ml. of ice water and filter rapidly. Add 0.15 g. of urea to destroy the excess nitrite, allow to stand for 5 minutes with stirring, and partially neutralize the mixture by the careful addition of 25 ml. of cold, approximately 3 N sodium carbonate solution. Stir in 10 g. of sodium acetate, rapidly filter any brownish precipitate which forms, and add the filtrate immediately to an ice-cold solution containing 0.49 g. of *p*-aminoazobenzene dissolved in 50 ml. of acetone with 100 ml. of alcohol and 20 ml. of saturated sodium acetate solution. Filter the brown precipitate immediately on a Buchner funnel, wash with ice water, then twice with 50 per cent aqueous alcohol containing a trace of ammonia, and finally with water. Dissolve the residue in 60-70 ml. of acetone containing 2 drops of dilute ammonium hydroxide that has previously been heated to 40-45° C., filter rapidly, and add water to precipitate the dye as a dark violet product.

**Detection of magnesium and cadmium.** Cation 2 $\beta$  dissolves in alcohol to yield a blue solution; and this yields a red color when added to a solution containing cadmium ions. In the presence of magnesium and potassium hydroxide, either a blue or a greenish-blue color forms, depending on the concentration of the magnesium ion. By means of these color reactions cadmium and magnesium can be detected.

**Reagent.** Add 0.01 g. of cation 2 $\beta$  to 100 ml. alcohol containing 2-3 drops of 2 N potassium hydroxide, and shake until dissolved.

**Procedure.** Make 10 ml. of the solution to be tested slightly acid with acetic acid, add 5-10 drops of the reagent, and then make distinctly alkaline with 2 N potassium hydroxide. With more than 15-20 $\gamma$  of magnesium per ml. a blue precipitate forms immediately, while with 2 $\gamma$  per ml. a blue precipitate forms only on standing. As little as 0.08 $\gamma$  magnesium per ml. can be detected with this reagent.

With 1 mg. cadmium per ml., red needles form, and with cadmium concentrations greater than 5-10 mg. per ml., sky-blue needles appear. With lower concentrations of cadmium, a red color appears.<sup>1</sup>

Magnesium and cadmium can be detected in the same sample by the following procedure:

**Procedure.** Add 0.25 g. of sodium potassium tartrate to 10 ml. of the solution to be tested, then add several drops of the reagent described above, and finally add 2 N potassium hydroxide until the solution is alkaline. A pink color



indicates cadmium. The cadmium lake is destroyed when the mixture is boiled; and, if magnesium is present, a greenish-blue color develops.

If metals other than cadmium and magnesium are present, add sufficient potassium cyanide to form complex cyanides before the addition of the reagent and potassium hydroxide.

It is possible to detect 0.002% of cadmium in one drop by means of a drop reaction.<sup>4</sup>

**Procedure.** Place 1 drop of reagent on a strip of filter paper, and then add a small drop of neutral or weakly acid solution to be tested, a crystal of Rochelle salt, and finally a drop of 20 per cent alcohol containing 2 N potassium hydroxide. If cadmium is present, a red fleck with a blue zone is formed.

Dwyer claims that this reaction is three times as sensitive as that with ordinary cadion.

One part of cadmium in 50 parts of lead and 100 parts of zinc can be detected by the following procedure:<sup>4</sup>

**Procedure.** Neutralize 5 ml. of the solution to be tested to blue litmus, and add 1 g. of Rochelle salt, 2 ml. of alcohol, and 3 drops of the reagent, and then add 2 N potassium hydroxide until the white precipitate disappears and a red color is formed.

Dwyer<sup>1</sup> explains the origin of the color with magnesium as due to the formation of a tautomer by the movement of the labile =NH hydrogen atom to the —NO<sub>2</sub> group. In this way a quinoid structure is formed, and this is stabilized by combination with magnesium hydroxide.

1. F. P. Dwyer, *Australian Chem. Inst. J. and Proc.* **5**, 197-200 (1938); *C.A.* **32**, 6578 (1938).
2. F. P. Dwyer, *Australian Chem. Inst. J. and Proc.* **5**, 32-6 (1938).
3. F. P. Dwyer, *Australian Chem. Inst. J. and Proc.* **5**, 338-46 (1938).
4. F. P. Dwyer, *Australian Chem. Inst. J. and Proc.* **5**, 37-40 (1938).
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**CADION 3β**      Synonym: Benzenediazoaminobenzene-4-azo-4'-nitrobenzene



**Use:** Detection of cadmium and magnesium.

Cadion 3β is a red crystalline solid. It melts with sudden immersion at 191° C. with decomposition. It dissolves readily in alcoholic alkali to form a dark blue solution. The compound is destroyed by mineral acids.

**Preparation:** Grind 1.21 g. of 4-nitro-4'-aminoazobenzene in a mortar with 20 ml. of 10 N hydrochloric acid. Pour the mixture into a beaker and heat to 90° C. for 2 minutes. Cool the mixture somewhat and pour on to 20 g. of powdered ice. Add 0.45 g. of sodium nitrite and allow the mixture to stand at 0° C. for 1 hour with frequent stirring. Then add 50 ml. of ice water and

stir well. Filter rapidly and add 0.2 g. of urea to destroy any unchanged nitrite, allow the mixture to stand until the reaction is complete, and almost neutralize by the addition of 50 ml. of 3 N sodium carbonate. Then add immediately to an ice-cold mixture of 0.5 g. of aniline, 50 ml. of water, 30 ml. of alcohol and 50 ml. of 3 N sodium acetate. An orange precipitate forms. Filter, wash with water, then with alcohol containing a drop of dilute ammonium hydroxide. Dissolve the product in hot acetone containing 2 drops of ammonium hydroxide, and finally precipitate with water.

**Detection of magnesium and cadmium.** Cadion 3 $\beta$  is similar to cadion 2 $\beta$  in most of its analytical characteristics, and like the latter may be used for the detection of magnesium and cadmium. Like cadion 2 $\beta$ , cadion 3 $\beta$  dissolves in alcohol to form a blue solution; and this turns red in the presence of cadmium. The sensitivity of the two reactions is about the same. Cadion 3 $\beta$  is perhaps the more stable, although cadion 2 $\beta$  is probably to be preferred. When cadion 3 $\beta$  is substituted for cadion 2 $\beta$  in the cadmium test, a red-violet precipitate forms from dilute solutions of cadmium salts, but in concentrated solutions the precipitate formed is bluish-red. In solutions containing tartrate, red needles are obtained in all cases. With magnesium hydroxide both dyes are adsorbed to form blue and blue-green needles. For details of use, refer to the section on cadion 2 $\beta$ , and simply replace this dye with cadion 3 $\beta$ .<sup>1-5</sup>

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2. F. P. Dwyer, *Australian Chem. Inst. J. and Proc.* **5**, 32-6 (1938).
3. F. P. Dwyer, *Australian Chem. Inst. J. and Proc.* **5**, 338-46 (1938).
4. F. P. Dwyer, *Australian Chem. Inst. J. and Proc.* **5**, 37-40 (1938).
5. F. P. Dwyer, *Australian Chem. Inst. J. and Proc.* **5**, 149-54 (1938); *C.A.* **32**, 6578 (1938).

### CHICAGO BLUE 6B(A)

$C_{34}H_{24}N_6O_{16}S_4Na_4$

Mol. Wt. 992.77

Color Index, 518.

$(NaO_3S)_2(OH)(NH_2)C_{10}H_3-N=N-C_6H_3(CH_3O)-$

$C_6H_3(CH_3O)-N=N-C_{10}H_3(OH)(NH_2)(SO_3Na)_2$

**Use:** Detection of magnesium.

The dye is a blue powder which dissolves in water with a pure blue color. It is insoluble in alcohol, but dissolves in sodium hydroxide with a blue-violet color and in sulfuric acid with a bluish-green color.

**Preparation:** Chicago Blue 6B(A) is prepared by coupling diazotized dianisidine with 2 molecular proportions of 1-amino-8-naphthol-2,4-disulfonic acid in an alkaline solution.

**Detection of magnesium.** The azo dye Chicago Blue 6B(A) may be used for the detection of magnesium.<sup>1-3</sup>

**Procedure.** Add 1-2 drops of 0.01 per cent aqueous solution of the dye to 1 drop of the solution to be tested, and follow with an excess of 2 N sodium hydroxide. The color of the dye in an alkaline solution is bluish-violet, but in the presence of magnesium the color is blue.

The test is sensitive to magnesium in the absence of nickel, cobalt, and chromium. As little as 0.0002 mg. of magnesium may be detected by comparison with a blank.

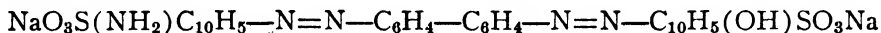
1. E. Eegriwe, *Z. anal. Chem.* **76**, 354-9 (1929); *C.A.* **23**, 2903 (1929).
2. Z. Karaoglanov, *Z. anal. Chem.* **119**, 16-55 (1940).
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## CONGO CORINTH

$C_{32}H_{21}N_5O_7S_2Na_2$

Mol. Wt. 697.61

Color Index, 375.



**Use:** Detection of cobalt, magnesium and nickel.

The compound is a greenish-black powder. It dissolves in water with a magenta-red solution, and in sulfuric acid to form a blue solution.

**Preparation:** Tetrazotize 4.6 g. of benzidine in the usual manner. Dilute the mixture to 500 ml. and add to a solution of 6.2 g. of sodium naphthionate and 6.3 g. of sodium carbonate in 200 ml. of water. Stir 30 minutes and add a solution of 2 g. of sodium carbonate, followed by a solution of 6.7 g. of 1-naphthol-4-sulfonic acid (sodium salt). Let stand overnight and heat to 80° C. the next day. Salt out the dye.<sup>1,2</sup>

**Detection of magnesium, cobalt, and nickel.** An alkaline solution of Congo corinth is red in color, but in the presence of magnesium, cobalt and nickel a brilliant violet coloration develops when the mixture is made alkaline.<sup>3</sup>

**Reagent.** Dissolve 0.1 g. of the dye in 100 ml. of water.

**Procedure.** Add 0.1-0.2 ml. of reagent to 10 ml. of the solution to be tested, and make alkaline with 1 ml. of 4 N sodium hydroxide. With magnesium, cobalt, or nickel, a brilliant violet color appears.

This reaction serves to detect 4 mg. of magnesium per liter; 0.5 mg. of cobalt per liter; and 1 mg. of nickel per liter. Manganese does not give a distinct reaction, but it interferes somewhat by the development of a brown color due to atmospheric oxidation. Beryllium, aluminum, zinc, lanthanum, and cadmium do not react, but they may interfere.

1. M. Lange, *Ber.* **19**, 1697 (1886).
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3. I. M. Kolthoff, *Mikrochem., Emich Festschr.* 180-90 (1930); *C.A.* **25**, 3267 (1931).

**DIAMINE PURE BLUE FF(C)** $C_{34}H_{25}N_6O_{18}S_3Na_3$ 

Mol. Wt. 813.54

Color Index, 518.

 $(NaO_3S)_2(OH)(NH_2)C_{10}H_8-N=N-C_6H_3(CH_3O)-$  $C_6H_3(CH_3O)-N=N-C_{10}H_3(OH)(NH_2)(SO_3Na)_2$ **Use:** Detection of magnesium and nitrite.

Diamine pure blue FF(C) is a blue powder, which dissolves in water with a blue solution. It also dissolves in sodium hydroxide to form a bluish violet solution, and in sulfuric acid to form a green solution. It is insoluble in alcohol.

**Preparation:** Couple tetrazotized dianisidine with 2 molecular weights of 1-amino-8-naphthol-2,4-disulfonic acid in an alkaline solution.

**Detection of magnesium.** The detection of magnesium with diamine pure blue depends upon the adsorption of the dye on precipitated magnesium hydroxide.

**Procedure.** Add 1-2 drops of a 0.01 per cent aqueous solution of the dye to 1 drop of the solution to be tested, and then add an excess of 2 N sodium hydroxide. An alkaline solution of the dye is bluish-violet, but in the presence of magnesium the color is blue.

This reagent is sensitive to magnesium in the absence of nickel, cobalt or chromium. By comparison with a blank, 0.0001 mg. of magnesium can be detected. In testing for 0.001 mg. of magnesium, the following do not interfere: 0.1 mg. of lead, stannic, aluminum, and beryllium ions; 0.05 mg. of zinc; and 0.001 mg. of ferric manganese ions. The following, interfere: 0.0005 mg. of manganese and ferric iron; and 0.001 mg. of chromium.

**Detection of nitrite.** Nitrites can be detected by the color formed when the dye is diazotized in an acid solution of a nitrite, and then coupled with a suitable reagent.

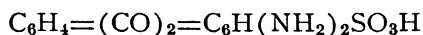
**Procedure.** To 2 ml. of the nitrite solution, add dropwise sufficient dye solution (10-50 mg. of dye per liter) to impart a perceptible color to the solution. This usually requires 1-5 drops. Then add 1 ml. of hydrochloric acid and after 10 minutes a small crystal of phenol. The blue color of the dye solution turns red at a dilution of 1:1,000,000.

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2. J. V. Dubsky and A. Okac, *Rec. trav. chim.* **46**, 296-302 (1927); *C.A.* **21**, 2627 (1927).
3. Z. Karaoglanov, *Z. anal. Chem.* **119**, 16-55 (1940).
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**1,2-DIAMINOANTHRAQUINONE-3-SULFONIC ACID** $C_{14}H_{10}O_5N_2S$ 

Mol. Wt. 318.28

Beil Ref. XIV, 766.

**Use:** Detection of cobalt, copper and nickel.

Determination of copper.

1,2-Diaminoanthraquinone-3-sulfonic acid is a solid which is readily soluble in water with the formation of a bluish-red solution.

**Preparation:** Mix one part of 1-bromo-2-aminoanthraquinone-3-sulfonic acid with 5 parts of aqueous ammonia (25 per cent  $NH_3$ ), and in the presence of a catalyst such as metallic copper, heat at  $100^\circ C.$  for 10 hours. Filter the product which separates, and purify by dissolving in water and precipitating with hydrochloric acid.<sup>1</sup>

**Detection of copper, nickel and cobalt.** Uhlenhuth<sup>2,3</sup> observed that an alkaline solution of 1,2-diaminoanthraquinone-3-sulfonic acid produced an intense blue color when added to solutions containing copper salts. The color is quite distinct at a dilution of 1.9 parts in 1,000,000 parts of solution and the extreme limit of detection of copper is 1.9 in 10,000,000. Uhlenhuth<sup>2,3</sup> attributes the color to the formation of a complex salt but Dubsky and Bencko<sup>4</sup> say that the copper compound is not a complex but an adsorption compound of 1,2-diaminoanthraquinone-3-sulfonic acid and a copper "hexolhydroxide" to which they assign the following structure,  $[(Cu(OH)_2)_3Cu](OH)_2$ .

Uhlenhuth's<sup>2,3</sup> reagent is prepared by dissolving 0.5 g. of 1,2-diaminoanthraquinone-3-sulfonic acid in 500 ml. of water and 40 ml. of 35 per cent sodium hydroxide solution. This reagent is red in color, and gives a blue coloration when not added in sufficient quantity to produce a violet color (due to a blend of the red and blue colors). The solution in which the blue coloration appears gives a greenish fluorescence in reflected light.

When a solution of a salt, such as ammonium chloride, ammonium nitrate or magnesium chloride is added to a copper salt solution, either before or after the addition of the reagent, a red color is formed instead of the usual blue color. Sodium chloride has no similar effect. When a solution of a copper salt and 1,2-diaminoanthraquinone-3-sulfonic acid is diluted with a large quantity of water, the blue is replaced with a red coloration.

Aqueous solutions of cobalt salts give a coloration similar to that produced with copper, and a blue precipitate if the cobalt concentration is sufficiently large. This reaction may be used to detect as little as 0.02 mg. of cobalt per ml. of solution.

The addition of ammonium hydroxide increases the sensitivity of the test to 0.0002 mg. of cobalt per ml. The sensitivity of the copper reaction is not appreciably affected by ammonium hydroxide. The coloration of the cobalt salt is not changed by dilution after the addition of 1,2-diaminoanthraquinone-3-sulfonic acid, and is not altered by the addition of ammonium chloride. Dilution

with water, therefore, and the addition of ammonium chloride may be used to differentiate between copper and cobalt. Sodium chloride has no influence on the color of the cobalt reaction.

Nickel salts yield a blue color with 1,2-diaminoanthraquinone-3-sulfonic acid. With this reaction as little as 0.2 mg. of the nickel per ml. can be detected. Unlike those of copper and cobalt, the nickel precipitate flocculates readily. The addition of a little 5 per cent ammonium hydroxide increases the intensity of the coloration with nickel to such an extent that 0.005 mg. of nickel per ml. can be detected. The addition of an equal volume of 5 per cent ammonium hydroxide and the subsequent addition of the reagent causes the blue coloration to change to red. This behavior provides a means of differentiating nickel from copper and cobalt. The influence of electrolytes, such as ammonium, magnesium and aluminum salts, on the color produced with copper and 1,2-diaminoanthraquinone-3-sulfonic acid may be nullified by the addition of a sufficient quantity of dilute sodium hydroxide solution. The blue coloration which has been altered to red by ammonium chloride may be restored by the addition of sodium hydroxide.

1,2-Diaminoanthraquinone-3-sulfonic acid has been used by various investigators,<sup>2,5-8</sup> for the detection of copper.

The following procedure may be used for the detection of copper in pure solutions of copper salts:<sup>8</sup>

**Reagent.** Dissolve 0.05 g. of 1,2-diaminoanthraquinone-3-sulfonic acid in 100 ml. of distilled water.

**Procedure.** Place a drop of the neutral or acid solution to be tested on a spot plate and mix with a drop of the reagent solution. Make alkaline with 1 N sodium hydroxide solution. The color changes from red to blue if copper is present. The sensitivity of this test is 0.02% of copper at a dilution of 1:2,500,000.

Ballaban<sup>8</sup> proposes the following test for detecting copper in the presence of nickel and cobalt:

**Reagents.** *1,2-Diaminoanthraquinone-3-sulfonic acid:* Dissolve 0.05 g. of 1,2-diaminoanthraquinone-3-sulfonic acid in 50 ml. of distilled water and 50 ml. of 1 N sodium hydroxide solution.

*Sulfite-thiocyanate solution:* Mix 2 parts of 1 N potassium thiocyanate with 1 part of sulfurous acid.

**Procedure.** Place a drop of the neutral or slightly acid solution to be tested on a strip of filter paper and dry at 90-100° C. Treat the spot with a drop of the sulfite-thiocyanate solution and again dry. Wash the paper with distilled water to remove nickel and cobalt salts. The copper remains fixed in the paper as insoluble copper thiocyanate. Change the wash water 6-8 times, and, after allowing the paper to soak for one-half minute each time, dry and apply to the spot a drop of the 1,2-diaminoanthraquinone-3-sulfonic acid solution. A blue color appears if copper is present.

Copper may be detected in metals by the following test:

**Reagent.** Dissolve 0.5 g. of 1,2-diaminoanthraquinone-3-sulfonic acid in 100 ml. of concentrated ammonium hydroxide, 360 ml. of water, and 40 ml. of 35 per cent sodium hydroxide.

**Procedure.** Apply a drop of hydrochloric or nitric acid to the metal to be tested, allow to stand for a few seconds, and take up the solution with a strip of filter paper. Make alkaline with 1-2 drops of dilute sodium hydroxide, and add 1 drop of reagent solution. Copper is detected by means of the blue color.

Copper can be detected when present in minute quantities in alloys of lead, tin and antimony. A drop of the reagent described above gives an intense blue color when applied directly to a plate of copper or cobalt without previous solution in acid. A scarcely perceptible blue color is obtained with nickel under the same conditions.

Sebor<sup>9</sup> has used the 1,2-diaminoanthraquinone-3-sulfonic acid-copper reaction for the determination of 0.04-0.2 mg. of copper. The addition of potassium hydroxide and 1,2-diaminoanthraquinone-3-sulfonic acid to copper sulfate solutions makes possible a matching of the colors obtained with those of standard copper sulfate solutions similarly treated within the range of concentration indicated above with a maximum error of  $\pm 1.2$  per cent. Addition of potassium hydroxide to 1,2-diaminoanthraquinone-3-sulfonic acid solution makes this reagent about one hundred times as sensitive as equivalent additions of ammonium hydroxide.

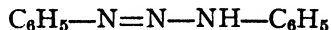
1. *Frdl.* 10, 588.
2. R. Uhlenhuth, *Chem.-Ztg.* 34, 887 (1910); *C.A.* 4, 3178 (1910).
3. R. Uhlenhuth, *Analyst.* 35, 453 (1910).
4. J. V. Dubsky and V. Bencko, *Z. anal. Chem.* 94, 19-20 (1933); *C.A.* 27, 5021 (1933).
5. G. Malatesta and E. Di Nola, *Boll. chim. farm.* 52, 819-23, 855-60 (1913); *C.A.* 9, 2200 (1915).
6. G. Gutzeit, *Helv. Chim. Acta.* 12, 713, 829 (1929).
7. D. Schenk, *Apoth. Ztg.* 28, 137 (1913); *C.A.* 7, 1464 (1913).
8. H. E. Ballaban, *Mikrochemie.* 27, 57-63 (1939); *C.A.* 33, 5771 (1939).
9. J. Sebor, *Chem. Listy.* 31, 419-20 (1937); *C.A.* 32, 3290 (1938).

## DIAZOAMINOBENZENE

$C_{12}H_{11}N_3$

Mol. Wt. 197.23

Beil. Ref. XVI, 687.



**Use:** Detection of cadmium.

Diazoaminobenzene is a golden-yellow crystalline solid. It melts at 98° C., and explodes when heated to 150° C. It is insoluble in water but dissolves readily in benzene, ether and hot alcohol.

**Preparation:** Dissolve 2 molecular weights of aniline in 3 molecular weights of hydrochloric acid. Cool well, and add a solution of 1 molecular weight of sodium nitrite to the cold mixture. Then add a concentrated solution of 2 molecular weights of sodium acetate in a concentrated aqueous solution.

Filter the yellow precipitate which forms, wash with water, dry on a porous plate, and recrystallize from alcohol.<sup>1,2</sup>

**Detection of cadmium.** Eegriwe<sup>3</sup> has used diazoaminobenzene in a sensitive test for cadmium:

**Procedure.** To a drop of the neutral solution to be tested, add 0.5 ml. of a 15 per cent solution of sodium carbonate ( $\text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$ ), 0.25 ml. of a solution of 0.5 g. of diazoaminobenzene in 100 ml. of acetone, and a few drops of chloroform. If cadmium is present, an orange-yellow color appears in the chloroform layer on shaking. As little as 0.2% of cadmium can be detected in this way.

Copper gives a greenish coloration and silver a brownish-yellow coloration when treated with diazoaminobenzene. Both of these metals, as well as cobalt and nickel, interfere with the cadmium test. The test can, however, be obtained with 3% of cadmium in the presence of 300% of lead, manganese, zinc, or magnesium.

1. B. Fischer, *Ber.* 17, 641 (1884).
2. B. Fischer and H. Wimmer, *Ber.* 20, 1581 (1887).
3. E. Eegriwe, *Z. anal. Chem.* 118, 98-100 (1939); *C.A.* 34, 2276 (1940).

## DIRECT GREEN B

$\text{C}_{34}\text{H}_{22}\text{O}_{10}\text{N}_8\text{S}_2\text{Na}_2$

Mol. Wt. 812.62

Color Index, 593.

**Use:** Detection of copper.

The compound is a dark powder. It dissolves in water with the formation of a dull-green solution, and in alcohol with a bluish-green solution. It also dissolves in sodium hydroxide solution with a yellowish-green color, and in sulfuric acid with a violet color.

**Preparation.** Couple tetrazotized benzidine in an alkaline solution with 1 molecular proportion of the product obtained by coupling diazotized *p*-nitroaniline with 1-amino-8-naphthol-3,6-disulfonic acid in an acid solution, and then couple with 1 molecular proportion of phenol.

**Detection of copper.** Direct Green B reacts with nearly neutral solutions of copper salts to give a distinct color change from blue-green to violet-pink.<sup>1</sup> The reaction should be carried out at 90° C., and the pH of the solution should lie between 6.0 and 9.0. Best results are obtained when the ratio of the concentration of the dye to copper is about 10:1, but satisfactory color changes may be observed when the dye: copper ratio ranges from 6:1 to 50:1.

The visual sensitivity of the reaction is 0.1 mg. of copper per liter, but by means of spectrophotometric measurements the sensitivity is about 0.004 mg. copper per liter, which is about the same as that obtained using sodium diethyl-dithiocarbamate.<sup>2</sup> Most anions have no effect upon the color, and no other metal



gives a violet-pink color. Neutral salts retard the reaction and reduce the intensity of the color. Potassium sulfate appears to have the most serious effect.

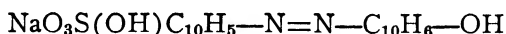
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### ERIOCHROM BLUE BLACK B(G)

$C_{20}H_{13}O_5N_2SNa$

Mol. Wt. 416.36

Color Index, 201.



**Use:** Detection of cobalt.

The dye occurs as a brownish-black powder. It dissolves in hot water with a violet solution, and in alcohol with a cherry-red solution. An aqueous sodium hydroxide solution is deep blue to cherry red, and a sulfuric acid solution is dark blue in color.

**Preparation:** Diazotize 12 g. of 1-amino-2-naphthol-4-sulfonic acid, and add to a solution prepared by dissolving 7.5 g. of  $\alpha$ -naphthol in 50 g. sodium hydroxide solution ( $d = 1.33$ ) at  $15^\circ C$ . After crystals form, add 250 ml. of water and neutralize with hydrochloric acid.

**Detection of cobalt.** Eriochrom blue black B(G) dissolves in water with a reddish-violet solution, and when this solution is treated with sodium nitrite and acetic acid it turns orange or yellowish-orange in color. If cobalt is present in the solution, however, the violet color persists. This reaction has been made the basis for a sensitive test for cobalt.<sup>1</sup>

In the absence of interfering substances, the test for cobalt is carried out as follows:

**Reagent.** Dissolve 0.01 g. of the dye in 50 ml. of water.

**Procedure.** To 1 drop of the solution to be tested add 5-10 drops of the reagent and 1 drop of 3.5 per cent sodium nitrite solution, and then acidify with a slight excess of 0.5 N acetic acid. A violet color remains if cobalt is present.

With 0.01 mg. of cobalt a violet color is obtained, and with 0.001 mg. of cobalt the color is bright violet, but as little as 0.0003 mg. of cobalt per ml. can be detected.

If considerable nickel is present, a transient brownish-yellow coloration is first observed, but on standing the violet color appears. Nickel should be removed before making the test.

1. E. Eegriwe, *Z. anal. Chem.* **82**, 150-4 (1930); *C.A.* **25**, 50 (1931).

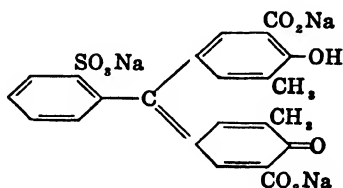
**ERIOCHROME CYANINE**

Synonym: Eriochrome cyanine R

 $C_{28}H_{15}O_9SNa_3$ 

Mol. Wt. 536.41

Color Index, 722.

**Use:** Detection and determination of aluminum.

Eriochrome cyanine is a brick red powder which dissolves in water with the formation of a red solution. The alcoholic solution is orange in color.

**Preparation:** Eriochrome cyanine is prepared by the condensation of benzaldehyde-*o*-sulfonic acid with *o*-cresotinic acid, the oxidation of the resulting product with nitrosyl sulfuric acid, and conversion to the sodium salt.

**Detection of aluminum.** The orange red solution of eriochrome cyanine is colored violet in the presence of aluminum. This reaction was proposed by Eegriwe<sup>1,2</sup> as the basis for a sensitive test for aluminum.

**Reagent.** Dissolve 0.1 g. of eriochrome cyanine in 100 ml. of distilled water.

**Procedure.** To 0.5 ml. of a solution containing the ions of the aluminum group, add an equal volume of sodium hydroxide solution and filter. Acidify the filtrate with acetic acid, and add 1 drop of the reagent. The orange-red reagent turns bluish-red in the presence of aluminum.

By means of the above test, 1γ of aluminum can be detected in the presence of 100 times as much lead, silver, mercury, cadmium, bismuth, antimony, tin, thorium, lanthanum, cerium, tungsten, molybdenum, uranium, titanium, zirconium, barium, strontium, potassium, sodium, lithium, rubidium, cesium, thallium and ammonium.

Copper, vanadium, and trivalent thallium interfere. Titanium, zirconium and thorium yield violet-red to blue-violet precipitates when present in fairly high concentrations, but the aluminum test can still be obtained. Phosphate, oxalate, fluoride, tartrate, silicate, fluoborate, silicofluoride, ferricyanide and chromate interfere.

Beryllium gives a test similar to that with aluminum, but the aluminum test may be obtained by suitable modification of the above procedure. In the presence of beryllium, add 0.2 N acetic acid to the heated solution which has been made alkaline, and then, after cooling, compare the resulting color with that of a pure beryllium solution.

Eegriwe<sup>1</sup> claims that eriochrome cyanine is a better reagent for aluminum than either morin or alizarinsulfonic acid if iron is present.

**Determination of aluminum.** The violet red color produced in the reaction between eriochromecyanine and aluminum may be used for the colorimetric determination of small quantities of aluminum.<sup>3-8</sup> The following method has been used by Alten and co-workers<sup>8</sup> for the determination of from 0.005 to 0.1 mg. of aluminum.

**Reagents.** *Eriochromecyanine reagent:* Dissolve 0.1 g. of eriochromecyanine in 100 ml. of water. This solution must be prepared daily.

*Buffer solution:* Mix 400 ml. of 5 N ammonium acetate, 200 ml. of 4 N sodium acetate and 25 ml. of 4 N acetic acid, and add sufficient water to make 1 liter of solution. The mixture formed by diluting 1 volume of this solution with 9 times as much water has a pH of 6.0.

*Separation of aluminum from phosphates and interfering cations.* Place 5 ml. of the solution to be analyzed and 5 ml. of pure water in a 25-ml. quartz tube. Add 2 ml. of a solution containing 7 g. of monopotassium phosphate in 1 liter of water and 1 g. of pure sodium hydroxide. Boil for 1 minute and add to the hot solution 2 ml. of a 10 per cent lithium chloride solution. Again boil for 1 minute, or until the odor of ammonia disappears. Cool, centrifuge, and decant off the clear centrifugate into a 100-ml. volumetric flask containing sufficient 10 per cent hydrochloric acid to make the solution acid after the alkaline centrifugate has been added. Wash the residue in the centrifuge tube with 2 ml. of water and add the clear washing to the main solution.

*Colorimetric determination.* To the solution in the flask add 10 ml. of the eriochromecyanine solution, and then add aluminum-free 2 N sodium hydroxide solution dropwise until the color is blue-violet, and then add dropwise with shaking sufficient 0.2 N acetic acid to cause the color to change first to yellow and then to a violet-red shade. Next add 10 ml. of the buffer solution and dilute to 100 ml. Mix well, and after 30 minutes measure the extinction of the test solution against a blank solution in the yellow-green (531  $m\mu$ ). The measured extinction when multiplied by 50 gives the approximate aluminum content in  $\gamma$ .

For an accurate determination, use the same procedure, but instead of 10 ml. of the reagent, use 5 ml. for 0.005-0.015 mg. of aluminum, 10 ml. for 0.015-0.050 mg. of aluminum, and 15 ml. for 0.05-0.1 mg. of aluminum.

The following procedure is described by Snell:<sup>8</sup>

**Reagents.** *Eriochromecyanine solution:* Dissolve 0.1 g. of reagent in 100 ml. of water.

*Buffer solution:* Dissolve 154 g. of ammonium acetate, 109 g. of sodium acetate trihydrate, and 6 g. of glacial acetic acid in water and dilute to 1 liter.

*Ammonium molybdate solution:* Dissolve 150 g. of ammonium molybdate in water and dilute to 1 liter, and then pour into 1 liter of 1:1 nitric acid.

*Uranyl acetate solution:* Dissolve 5 g. of uranyl acetate in 100 ml. of 5 per cent acetic acid solution.

**Procedure.** Use a quantity of sample which contains 0.01-0.001 mg. of aluminum. Ash carefully in a platinum dish if organic matter is present. Add 0.5 ml. of concentrated sulfuric acid to the carbon-free ash and heat until fumes of sulfur trioxide appear.

If the ash contains silicates, add 1 g. of a 1:1 mixture of sodium and potassium carbonates and heat until the mass is fused. Keep the mass molten for 10-15 minutes, allow to cool, and add 2 ml. of water. Allow to stand until everything which will dissolve has passed into solution, and filter. Treat the residue with three 2-ml. portions of 1:4 nitric acid, and transfer the resulting solution to a quartz flask. Boil to expel carbon dioxide, and precipitate any phosphates which are present with the ammonium molybdate solution.

Transfer the solution of the sample to a test tube and dilute to about 8 ml. with water. A blank solution and a standard containing about the same quantity of aluminum as the unknown are then each treated with 2 ml. of 0.1 per cent monopotassiumphosphate solution and diluted to about 8 ml. Then add dropwise, with stirring, 2 ml. of the ammonium molybdate solution to the sample, standard and blank. Allow to stand for 1 hour, shake, and after 10 minutes add 2 ml. of 50 per cent ammonium nitrate solution. Again shake and after standing for an additional hour filter each solution into a 20-ml. quartz test tube. Wash each filter with 2 ml. of 2 per cent ammonium nitrate solution.

Add 2 ml. of the uranyl acetate solution and 2 drops of bromothymol blue indicator solution. Add 1:3 ammonium hydroxide solution dropwise and with stirring until a greenish-color is obtained, and then a yellow-white precipitate of molybdic acid and ammonium uranate is formed. Aluminum is carried down with these precipitates. Allow to stand for 2 hours and centrifuge. Decant the upper layer and dissolve the residue in 10 ml. of a 5 per cent sodium carbonate solution.

If brown precipitates remain due to the presence of iron and manganese, the mixture should again be centrifuged and the liquid decanted into 100-ml. volumetric flasks. Wash the residues with 2-ml. portions of water, and again centrifuge and add the liquids to the flasks. Dissolve the precipitates in 2-ml. portions of 1:20 hydrochloric acid and dilute to 5 ml. Add to each 2 ml. of 2 N sodium hydroxide and boil. Cool, centrifuge, and decant these liquids into the flasks. If only very little precipitate remains after treatment with the sodium carbonate solution, transfer the solutions to the flask without the additional steps for the separation of aluminum from iron and manganese.

Now shake the mixtures containing the sample, standard and blank to expel carbon dioxide, and to each add 15 ml. of eriochromecyanine solution. Carefully add 2 N sodium hydroxide until the orange-red color changes to a dark violet-red and a precipitate of ammonium uranate and molybdic acid is formed. Add 5 per cent hydrochloric acid dropwise until the precipitate just redissolves, leaving only a faintly turbid mixture. Then add 20 ml. of the buffer solution and dilute to 100 ml. Compare the color obtained in the unknown with that of the standard which has been similarly prepared. The color comparison should be made within 1 hour, using a yellow-green filter.

This method gives results which are accurate to about 6 per cent if iron and manganese are present, and somewhat better results when these metals are absent. The color is changed by the presence of nickel, zinc, manganese, chromium and iron when aluminum is present.<sup>4</sup> The effect of iron or manganese is said to be seven times as great as that of aluminum, and that of magnesium to be twice that of aluminum. Phosphates and organic materials decrease the color. Interfering substances may be removed, or suitable steps taken to correct the effect which they produce.

The color formed in the reaction between aluminum and eriochrome cyanine is influenced by the pH of the reaction mixture. A given quantity of aluminum at a pH of 4.6-5.6 gives with a 0.1 per cent aqueous solution of eriochrome cyanine a color lake in the presence of a sodium acetate-acetic acid buffer solution. This lake has a much stronger color than that obtained with a sodium acetate-ammonium acetate-acetic acid buffer solution. According to Millner<sup>9</sup> it appears that the aqueous solution of eriochrome cyanine at the above pH consists of 2 molecular species, and for the formation of a color lake it is predominantly one of these which is involved.

Klinger and co-workers<sup>10</sup> have reported that the photometric method of determining aluminum with eriochrome cyanine is the most sensitive method for the analysis of aluminum in iron and steel.

Rauch<sup>11</sup> has described the following method for the determination of aluminum in magnesium alloys.

**Procedure.** Dissolve the alloy in such volume of solution that 100 ml. contains about 80 mg. of aluminum. Transfer 5 ml. of this solution to a 200-ml. volumetric flask, and add 20 ml. of a 0.1 per cent solution of eriochrome cyanine in 0.1 per cent acetic acid, and 10 ml. of a solution containing 40 per cent of sodium acetate and 9.6 per cent acetic acid. Dilute to the mark and allow to stand for 30 minutes for the development of the violet color. Measure in a photoelectric colorimeter.

Millner and Kunos<sup>12</sup> have used eriochrome cyanine for the determination of traces of aluminum in tungsten and tungstic acid. Trenel and Alten<sup>7</sup> have used a similar procedure for the determination of aluminum in plants.

Bischof and Geuer<sup>15</sup> have used eriochrome cyanine for the determination of aluminum in aluminum alloys containing zinc and copper or zinc and iron.

Werner<sup>13</sup> and Steinhauser<sup>14</sup> have used eriochrome cyanine for the colorimetric determination of aluminum oxide in aluminum.

**Procedure.** According to the aluminum oxide content, treat 0.5-5.0 g. of the mixture with 200-300 ml. of methyl alcohol and 20 ml. of pure bromine. Allow the mixture to stand for 1-1.5 hours until the reaction has subsided, and then heat for an additional 3 hours, or allow the mixture to stand overnight. Filter, and wash the residue with methyl alcohol. Ignite in a platinum dish and remove silica in the usual manner with hydrofluoric and sulfuric acids. Fuse

with potassium pyrosulfate, dissolve the melt in warm water, and dilute to exactly 100 ml. Mix well and neutralize 10 ml. of the solution to phenolphthalein with sodium hydroxide, and acidify with 10 drops of 5 per cent hydrochloric acid. Add 20 ml. of an acetate buffer of pH 6.0, and 10 ml. of a 0.1 per cent eriochrome cyanine solution. Dilute to 100 ml. and allow to stand for 15 minutes. Then measure the color in a Pulfrich photocolormeter using a mercury lamp and an Hg 578 filter. The per cent of aluminum can be read from a standard curve prepared with solutions of aluminum sulfate of known aluminum content.

1. E. Eegriwe, *Z. anal. Chem.* **76**, 438-43 (1929); *C.A.* **23**, 2901 (1929).
2. E. Eegriwe, *Z. anal. Chem.* **108**, 268-9 (1937); *C.A.* **31**, 3814 (1937).
3. F. Alten, H. Weiland and E. Knippenberg, *Z. anal. Chem.* **96**, 91-8 (1934); *C.A.* **28**, 2294 (1934).
4. F. Alten, B. Wandrowski and E. Hille, *Angew. Chem.* **48**, 273-5 (1935); *C.A.* **29**, 5037 (1935).
5. W. Koch, *Arch. Eisenhüttenw.* **12**, 69-80 (1939); *C.A.* **33**, 5318 (1939).
6. O. Schams, *Mikrochemie.* **25**, 16-46 (1938).
7. M. Trenel and F. Alten, *Angew. Chem.* **47**, 813 (1934).
8. F. D. Snell and C. T. Snell, *Colorimetric Methods of Analysis*, Vol. I, p. 271. D. Van Nostrand, New York (1936).
9. T. Millner, *Z. anal. Chem.* **113**, 83-118 (1938); *C.A.* **32**, 6970 (1938).
10. P. Klinger, W. Koch and G. Blaschczyk, *Tech. Mitt. Krupp Forschungs Ber.* **3**, 255-73 (1940); *C.A.* **35**, 1726 (1941).
11. A. Rauch, *Z. anal. Chem.* **124**, 17-25 (1942); *C.A.* **37**, 5332 (1943).
12. T. Millner and F. Kunos, *Magyar Kem. Egyesulete, Szakmai Egyesulete Kozlomenyek.* **68-75** (1939); *C.A.* **36**, 5439 (1942).
13. O. Werner, *Z. anal. Chem.* **121**, 385-98 (1941); *C.A.* **36**, 5110 (1942).
14. K. Steinhäuser, *Aluminum.* **24**, 176-8 (1942); *C.A.* **37**, 3016 (1943).
15. E. Bischof and G. Geuer, *Metall u. Erz* **41**, 57-63 (1944); *C.A.* **39**, 674 (1945).

## ERIOCHROME RED B(G)

$C_{20}H_{15}O_5N_4SNa$

Mol. Wt. 446.38

Color Index, 652.

**Use:** Detection of cobalt.

**Preparation:** Dissolve 9 g. of 1-phenyl-3-methyl-5-pyrazolone, 6 g. sodium hydroxide ( $d = 1.38$ ), and 7.5 g. of sodium carbonate in 250 ml. of water, and to this solution add slowly and with stirring 12.5 g. dry 1-diazo-2-naphthol-4-sulfonic acid. Allow to stand several hours and salt out.

The dye is a brownish-red powder. It is soluble in hot water with a yellowish-red color. It dissolves in sodium hydroxide with an orange-yellow solution, and in sulfuric acid with a magenta-red color.

**Detection of cobalt.** An aqueous solution of the pyrazolone dye, eriochrome red B(G), becomes reddish-yellow when treated with sodium nitrite and acetic acid. When cobalt is present, however, the color is orange. This reaction

has been made the basis for a sensitive test for cobalt.<sup>1</sup> The procedure must provide for the removal of nickel.

**Reagent.** Dissolve 0.01 g. of the dye in 50 ml. of water.

**Procedure.** To one drop of a nickel solution containing cobalt, add 1.5-2.0 ml. of 5 N sodium hydroxide containing 10 per cent glycerol by volume. Boil, filter, and make the filtrate acid with hydrochloric acid. Neutralize with solid sodium bicarbonate, add 5-10 drops of the dye solution, and then 2 drops of 3.5 per cent aqueous sodium nitrite solution, and finally make acid with 0.5 N acetic acid. As little as 0.0005 mg. of cobalt may be detected in a solution originally containing 5 mg. of nickel in 5 ml. of solution. The sensitivity may be increased to 0.0002 mg. by comparison with a blank.

Chromic and vanadate ions give only a transient orange color with the eriochrome red reagent. The color caused by chromic ions soon disappears, but the color due to vanadates remains some time, depending on the quantity of vanadate present.

1. E. Eegriwe, *Z. anal. Chem.* **82**, 150-4 (1930); *C.A.* **25**, 50 (1931).

## ERYTHROSIN

$C_{20}H_6O_5I_4Na_2 \cdot H_2O$

Mol. Wt. 897.95

Color Index, 773.

**Use:** Detection of mercury.

The dye occurs as a brown powder. This dissolves in water to form a cherry-red solution.

**Preparation:** Dissolve 6 g. of fluorescein in a hot solution of 8 g. of sodium hydroxide ( $d = 1.33$ ) and 60 ml. of water, and mix with a boiling solution of 24 g. of iodine in 27-28 g. of sodium hydroxide solution ( $d = 1.33$ ) and 60 ml. of water. Then add slowly with stirring 25 g. of glacial acetic acid and boil the resulting mixture. Neutralize with 17 g. of sodium hydroxide solution ( $d = 1.33$ ) and quickly add a mixture of 25 ml. of water and 25 g. of hydrochloric acid. Dilute to 600 ml. with water, boil, allow to settle, and filter. Boil the residue with 10 g. of hydrochloric acid and filter, and then boil with 300 ml. of water and filter again. Convert to the alkali salt.

**Detection of mercury.** Erythrosin may be used for the detection of mercury.<sup>2</sup>

**Procedure.** To 5 ml. of solution of mercurous ion, add a few drops of an aqueous solution of the dye, and then precipitate with 1 N sulfuric acid. A pink precipitate forms in solutions containing 10 mg. of mercurous ion per ml.

1. J. W. Smith and H. E. Rogers, *J. Chem. Ed.* **16**, 143-4 (1939); *C.A.* **33**, 3287 (1939).

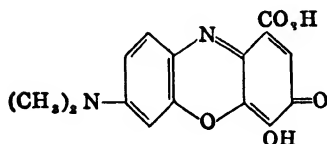
## GALLOCYANINE

 $C_{15}H_{12}O_5N_2$ 

Mol. Wt. 300.26

Beil. Ref. XXVII, 438.

Color Index, 883.



**Use:** Detection of aluminum, antimony, bismuth, cadmium, chromium, cobalt, lead, magnesium, manganese, mercury, nickel, silver, tin and zirconium.

Gallocyanine is a green crystalline solid, which is insoluble in cold water but slightly soluble in hot water. It is soluble in alcohol and glacial acetic acid. It dissolves in solutions of alkali carbonates with a reddish color, and in concentrated hydrochloric acid with a clear red color. The aqueous solution of the dye is blue.

**Preparation:** Mix 75 g. of gallic acid, 35 g. of *p*-nitrosodimethylaniline hydrochloride and 850 g. of methyl alcohol, and boil under reflux with the gradual addition of 85 g. of *p*-nitrosodimethylaniline hydrochloride during a period of 4 hours. Continue the boiling until a drop of the mixture when placed on filter paper yields a deep violet spot without a yellow rim. Then remove the alcohol by distillation, boil the product with water and filter.

**Reactions with metals.** Gallocyanine forms reddish-violet solutions in acids and blue-violet solutions in alkalis. These solutions have been used by Dubsy<sup>1,2</sup> in color reactions for the detection of several metals. A slightly acid, 0.005 N solution of gallocyanine when treated with a 0.1 N mercurous salt solution forms immediately a pale blue precipitate of gallocyanine adsorbed on finely divided mercury. With trivalent antimony solutions, blue  $(C_{15}H_{11}O_5N_2)SbCl(OH)$  or  $(C_{15}H_{11}O_5N_2)_2SbCl \cdot 15H_2O$  is obtained, but no visible reaction occurs immediately with silver, lead, copper, ferric iron or aluminum.

A solution of gallocyanine is decolorized by stannous chloride. On standing for 12 hours a brown precipitate is obtained with silver, a dark blue precipitate with nickel, a violet precipitate with lead, and a pale blue precipitate with bismuth. Other cations do not react. In a strongly acid solution, the only reactions are with mercurous and antimony salts.

In dilute ammoniacal solutions of gallocyanine, bluish-violet precipitates are immediately obtained with mercurous, bismuth, and manganese salts, a pale blue precipitate forms with mercurous salts, a blue precipitate with lead, antimony and chromium, and a dark brown precipitate with ferric iron. On standing for 12 hours a gray precipitate is obtained with silver, a violet precipitate with cadmium, a green precipitate with cobalt, a bluish-violet precipitate with nickel, and blue precipitates with magnesium and aluminum.



With lead the compound  $C_{16}H_{11}N_2Pb_2(OH)_3$  is formed. This substance is soluble in acids, but is insoluble in water, ethyl alcohol, ammonia and ether.

Gallocyanine is a useful precipitant for trivalent antimony, and may be used for the detection of as little as 30 $\gamma$  of this metal.

**Detection of lead.** Lead in neutral solutions, or as the hydroxide, can be detected by the formation of a violet lake by the addition of a solution of gallocyanine. In this way 0.3 $\gamma$  or lead can be detected.<sup>3,6</sup>

**Procedure.** Place a drop of the solution to be tested on a strip of filter paper and add a drop of a 1 per cent aqueous pyridine solution, and then add a 0.1 per cent solution of gallocyanine. Wash the spot with successive drops of 1 per cent pyridine. If lead is present a violet stain forms on the paper.

If other metals are present, the lead should be precipitated as the sulfate on the paper before treatment with gallocyanine. In this way 2-3 $\gamma$  of lead may be detected in the presence of 10-15 times as much silver, bismuth, copper and cadmium.

When carried out on a spot plate, this method is capable of detecting 0.36 $\gamma$  of lead at a concentration of 1:83,300. Rossi and Serantes<sup>7</sup> have used gallocyanine for the detection of lead in alloys of tin, bismuth, and lead.

**Detection of zirconium.** Solutions of gallocyanine in dilute acid are pink to red in color, but these turn blue in the presence of zirconium. This reaction has been used by Pavelka<sup>4</sup> for the detection of small quantities of zirconium:

**Procedure.** To 1 ml. of the solution to be tested add 0.2-0.3 ml. of 2 N hydrochloric acid, and add a quantity of aqueous gallocyanine solution which is just sufficient to impart a pink coloration to a blank test with dilute hydrochloric acid. Warm on a water-bath. A blue color appears if zirconium is present. If aluminum, thorium, beryllium or cerium is present, the unknown solution should contain 10 per cent of concentrated hydrochloric acid.

Titanium interferes, but 20 $\gamma$  of zirconium can be detected in the presence of 2000 times as much aluminum or cerium and 1000 times as much thorium. Forty  $\gamma$  of zirconium can be detected in the presence of 500 times as much beryllium.

Zirconium may be separated from thorium as the arsenate.<sup>5</sup> When such a precipitate is formed in the presence of gallocyanine a highly colored product is obtained which makes possible the detection of smaller quantities of zirconium than is possible by precipitation with the arsenate alone:

**Procedure.** Mix the solution to be tested with a crystal of gallocyanine, and if the solution is not acid, treat with 0.2-0.3 ml. of 1:4 hydrochloric acid. Heat almost to boiling and mix with 1 ml. of 4 per cent sodium arsenate solution and warm for a short time on a water-bath. Dilute with about one-half volume of alcohol to dissolve any gallocyanine which remains, and boil for a short time. To make the precipitate perceptible, filter off the solution, using an Emich filter

stick. In this way the precipitate is concentrated on a small filter surface. Wash with 1 ml. of alcohol and allow to dry.

With 20% of zirconium, the arsenate test is negative, but with the same quantity of zirconium and in the presence of galloxyanine a blue-black precipitate is obtained. By the use of the Emich filter stick, 2-3% of zirconium can be detected by the color of the filtering surface.

Aluminum and beryllium do not interfere in this test. If cerium is present, the solution should be strongly acid, since in dilute acid cerium also yields an insoluble arsenate. The only modification necessary in the above test if cerium is present is to increase the acid concentration to 0.3 ml. of concentrated hydrochloric acid per ml. of solution. Interference due to thorium is eliminated in the same way.

Zirconium may also be detected with galloxyanine and *m*-nitrobenzenearsonic acid. With these reagents 5% of zirconium is detectable:

**Procedure.** Mix a few drops of the zirconium solution containing 0.2-0.3 ml. of concentrated hydrochloric acid per ml. with a few drops of an aqueous solution of *m*-nitrobenzenearsonic acid. An immediate turbidity forms with zirconium. The test is sensitive to 1 part in 1,000,000 by carrying out the precipitation in the presence of galloxyanine.

1. J. V. Dubsky, *Chem. Listy*, **34**, 1-2 (1940); *C.A.* **34**, 5370 (1940).
2. J. V. Dubsky and L. Chodak, *Collection Czech. Chem. Commun.* **11**, 523-5 (1939); *C.A.* **35**, 2445-46 (1941).
3. F. Pavelka, *Mikrochemie*, **7**, 301-4 (1929); *C.A.* **24**, 3965 (1930).
4. F. Pavelka, *Mikrochemie*, **8**, 345-51 (1930); *C.A.* **25**, 892 (1931).
5. L. Moser and R. Lessnigg, *Monatsh.* **45**, 323 (1924).
6. J. V. Dubsky and J. Trtilek, *Chem. Obsor.* **9**, 68-9 (1934); *C.A.* **28**, 5001 (1934).
7. L. Rossi and A. T. Serantes, *Rev. asoc. bioquim. argentina*, **11**, 323-5 (1944); *C.A.* **39**, 3757 (1945).

## HEMATEIN

$C_{16}H_{12}O_6$

Mol. Wt. 300.26

Beil. Ref. XVIII, 227.

**Use:** Detection of bismuth, lead, molybdenum, and tin.

Determination of lead.

Hematein is obtained as reddish-brown crystals, having a yellowish-green, metallic luster. It melts above 200° C. It is soluble in about 1700 parts of water, is only slightly soluble in alcohol and ether, is insoluble in benzene and chloroform, but dissolves freely in ammonia with a brownish-violet color, and in dilute sodium hydroxide with a bright red color.

**Preparation:** Prepare a suspension of 15 g. of finely powdered hematoxylin in 150 ml. of water and 15 ml. of concentrated ammonia, and through this mixture pass a rapid stream of air for six hours with cooling. Pour the mixture into 250 ml. of warm 10 per cent acetic acid.

**Detection and determination of lead.** Hematein produces a dark blue precipitate when added to an aqueous solution containing lead salts.<sup>1</sup> This precipitate is easily filtered, and on heating in a crucible yields metallic lead.

**Procedure.** To 100 ml. of solution to be tested, add 0.5-1 ml. of a clear red, freshly prepared solution obtained by dissolving 0.5 g. of hematein in 1 liter of hot water. With lead salts a blue-precipitate forms.

This reaction is particularly suitable for detecting lead in drinking water. The sensitivity of the reaction is 1:2,000,000. Copper and zinc also give blue colors with hematein, but this is not troublesome in the analysis of drinking water, since these elements are seldom present.

Many metals react with hematein to give highly colored products. Some of these are listed in Table 52.

TABLE 52.—REACTIONS WITH HEMATEIN

Salt	Color
Potassium antimonate	Cherry-red
Potassium dichromate	Dark Brown
Ammonium chloride	Yellow
Sodium sulfate	Yellow
Alum	Violet
Ferrous sulfate	Black
Potassium ferrocyanide	Purple-red
Chrome alum	Yellow-brown
Magnesium sulfate	Yellow-red
Silver nitrate	Brown
Mercuric nitrate	Yellow
Bismuth nitrate	Violet
Nickel nitrate	Brown
Tin chloride	Violet

1. M. R. Moffatt and H. S. Spiro, *Chem.-Ztg.* 31, 639 (1907).

2. J. V. Dubsky and J. Trtilek, *Chem. Obzor.* 9, 142-4 (1934); *C.A.* 28, 7194 (1934).

## HEMATIN

Synonym: Phenodin

**Use:** Detection of copper.

Hematin ( $C_{32}H_{32}O_4N_4Fe$ , mol. wt. 633.49) is a blue-black powder, which decomposes at 200° C. without melting. It is insoluble in water, alcohol, chloroform and ether; but it dissolves in alkalis or ammonia to form red solutions.

**Detection of copper.** Duval<sup>1</sup> has replaced hematoxylin with hematin as a reagent for the detection of copper. The reactions are similar, although the hematin reaction is less sensitive than that with hematoxylin.

1. C. Duval, *Compt. rend.* 211, 280-2 (1940); *C.A.* 36, 55 (1942).

**HEMATOXYLIN**

Synonym: Hydroxybrasilin

 $C_{16}H_{14}O_6 \cdot 3H_2O$ 

Mol. Wt. 356.32

Beil. Ref. XVII, 219.

**Use:** Detection of aluminum, ammonia, copper, mercury, lead, cadmium, iron, bismuth, molybdenum, tin and chromium, arsenic, zinc and nickel.

Determination of aluminum, copper and iron.

Hematoxylin is obtained from the heartwood of logwood. It is a white to yellowish crystalline solid, which turns red on exposure to light. The melting point is variously stated at 100-120° C. and 140° C. The compound is slightly soluble in cold water and ether, but is soluble in hot water, hot alcohol, alkali hydroxides, and glycerol. Solutions of this compound darken on standing.

**Reactions with metals.** Solutions of hematoxylin, or logwood extract, react with solutions of various cations to yield colored compounds. Some of these, such as those formed in reactions with copper, aluminum and iron, may be used for the detection of these metals. A summary of these reactions is given by Gutzeit,<sup>1</sup> who has used this reagent for detecting various metals by means of spot tests. His procedure consists of impregnating filter paper with a solution of hematoxylin and then spotting this paper with a drop of a solution containing the metallic ion. His results are given in Table 53.

TABLE 53.

Ion	Color
Mercury	Brown-red
Lead	Lilac-violet
Copper	Violet
Bismuth	Violet, surrounded by a rose ring
Cadmium	Yellowish-rose
Arsenic	Mauve-rose
Stannous	Violet-red
Iron	Violet-brown
Chromate	Violet-black
Zinc	Brown-rose
Aluminum	Violet
Nickel	Pale rose

**Detection of copper.** Logwood extract, or hematoxylin, reacts with solutions of copper salts to produce a dark blue color. This reaction is of extraordinary delicacy and may be used for the detection of copper. A blue color is obtained with solutions containing only 0.0000001 per cent of copper, which is 1000 times as sensitive as the well-known ferrocyanide reaction.<sup>1-3,17,18</sup> Duval<sup>4</sup> has suggested a modification of this reaction, based upon the formation of a colored complex of copper with hematoxylin and gelatin or cellophane. The following procedure is used.

**Procedure.** Treat a clear gelatin-covered glass plate, or a strip of thick colorless cellophane for 10 minutes with a 1.0 per cent solution of hematoxylin, and then wash with distilled water and dry. Place upon the resulting film, which is now yellow in color, a drop of the solution to be tested. When the spot is examined under 75-250-fold magnification, a gray to green central zone is first observed if copper is present, and this slowly turns to violet, and after 2-3 minutes a sky blue spot appears surrounded by a reddish outer ring. As little as 0.03% of copper can be detected with this procedure.

Chloride, sulfate and nitrate do not interfere. Nickel, cobalt, iron, zinc, manganese, cerium, uranyl, vanadyl, titanium, mercury, tin, thallium, lead, bismuth, cadmium, aluminum, chromium, chromate, beryllium, sodium, potassium, calcium, barium, strontium, platinum, cyanide, thiocyanate, ferrocyanide and ferricyanide ions usually give a green color, but if these ions are not present in too great a quantity they do not interfere seriously with the copper test. Peranganate causes a golden yellow spot. Silver salts give a bright red spot, and gold salts a violet spot. Even these ions, however, do not prevent the detection of copper in mixtures. In the presence of ammonia the color is dark violet. The most satisfactory test is obtained in solutions having a pH of 6.2.

**Determination of copper.** The color produced in the reaction between copper ions and hematoxylin has been used by Goday<sup>6</sup> for the colorimetric determination of copper.<sup>13</sup>

**Detection of iron.** A violet-red to violet-blue color is obtained when a 5 per cent alcoholic solution of hematoxylin is added to a solution containing an iron salt. These colors are given by ferric and ferrous compounds of organic and inorganic acids. Other iron-containing organic compounds such as albuminoids do not give this reaction. As little as 1 part of ferrous iron in 10,000,000 parts of solution may be detected by this color.<sup>1,7,19,20</sup>

**Determination of iron.** Goday<sup>6</sup> has proposed a method for determining iron colorimetrically based upon the formation of the violet to red color with a solution of hematoxylin.

**Detection of bismuth, molybdenum and tin.** Strips of filter paper which have been impregnated with an alcoholic extract of logwood and dried in an atmosphere free of ammonia give characteristic color reactions with many ions in neutral or almost neutral solutions, but in only a few cases are these colors persistent in weakly acid solutions.<sup>6</sup> Among the ions which yield colors which are stable in acid solutions are the following:

(a) Bismuth salts give an intense violet color with hematoxylin, and this is stable in a quite strongly acid solution.

(b) Arsenic, antimony, and tin also yield violet colors with hematoxylin, but in more strongly acid solutions may yield only a reddish spot.

(c) Molybdenum gives a blue color which is stable in acids.

To detect tin, molybdenum and bismuth use the following procedure:<sup>6</sup>

**Procedure.** Treat a little of the mineral or alloy to be analyzed repeatedly with nitric acid and a few crystals of sodium sulfate, and heat until the oxides of nitrogen are no longer evolved. Do not evaporate to dryness. Dissolve the residue in a little water, filter, and wash the residue with nitric acid, and boil with saturated tartaric acid, and finally boil for a few minutes with a little water and a few fragments of potassium or sodium hydroxide. Apply a drop of this solution to filter paper impregnated with hematoxylin. If no tin is present, the blue color imparted to the hematoxylin paper by the above solution will disappear completely when moistened with nitric acid, but if tin is present a violet stain remains.

Treat a portion of the original filtrate, containing bismuth, arsenic and molybdenum, with a few drops of ammonia, sodium phosphate in excess, and sodium chloride, and then warm to 40° C. and filter. Place a drop of the filtrate on the hematoxylin paper. If bismuth is present, a violet color appears. In another portion of the original filtrate, precipitate bismuth with sodium hydroxide; and, if molybdenum is present, a blue stain will form when the solution is placed on hematoxylin paper, and this does not disappear when the spot is moistened with nitric acid.

**Detection of chromium.** A violet black color is obtained when logwood extract is heated with a neutral solution of a chromate.<sup>21,22</sup> Wildenstein<sup>8,9</sup> has based a method for the detection of chromium upon this reaction. The test is sensitive to 1 part of chromate in 500,000,000 parts of solution.

**Detection of aluminum.** Hematoxylin reacts with neutral solutions of aluminum salts to form a blue color. This reaction is used for the detection of aluminum.<sup>10,23,24</sup> As little as 0.3γ of aluminum can be detected by a drop reaction.

**Determination of aluminum.** The violet color obtained when hematoxylin is added to solutions containing small quantities of aluminum salts may be used for the colorimetric determination of aluminum in water.<sup>10-12,14</sup> The colored aluminum compound is formed in samples of water in which the pH is adjusted to 8.2-8.3, and then the mixture is acidified to pH 4.5. This method, described by Hatfield,<sup>10</sup> is applicable to routine analysis and is particularly suited to the determination of aluminum in water. It is accurate to 0.1 p.p.m. of aluminum.

**Procedure.** To 50 ml. of the water to be analyzed, contained in a tall-form Nessler tube, add 1 ml. of saturated aqueous ammonium carbonate and 1 ml. of a solution prepared by dissolving 0.1 g. of hematoxylin in 100 ml. of boiling water. Mix by inverting the tube two times and then allow the mixture to stand for 15 minutes. Acidify by adding 1 ml. of 30 per cent acetic acid, and compare with standards similarly and simultaneously prepared. The standards should contain 0.0-1.0 p.p.m. of aluminum. A preliminary acidification of the sample, followed by neutralization, is recommended to insure all aluminum being in the form of the aluminum ion.<sup>24</sup>

There is little interference in this procedure with ions other than iron; and Naumann,<sup>11</sup> who recommends the procedure of Hatfield, suggests that if more than 1 mg. of iron is present, interference from this source may be eliminated by adding a corresponding quantity of iron to the standard solutions. Only aluminum in ionic form may be determined by this method. This method may be used to determine as little as 0.1 mg. of aluminum, and is useful for the examination of water that has been treated with alum or aluminum sulfate. The hematoxylin method is also suitable for the determination of aluminum in filtered soil extracts.<sup>25</sup>

The following procedure has been suggested for the determination of small quantities of aluminum contained in alkalis, such as sodium or potassium hydroxide.<sup>12</sup>

**Procedure.** Dissolve 2 g. of the alkali to be analyzed in 10 ml. of water contained in a silver cup. Add 6-7 ml. of 1:1 hydrochloric acid and 2-3 drops of phenolphthalein, and then just decolorize with the dilute hydrochloric acid, and then add 0.1-0.2 ml. in excess. Transfer the solution to a 100-ml. colorimeter tube, stopper, and shake, and add N sodium hydroxide until a pink color appears, and then add 1 ml. in excess. Dilute with water to 40 ml., add 0.1 per cent sodium acetate, mix well, and add a 1 per cent solution of hematoxylin. Dilute with water to 50 ml., add 1 ml. of acetic acid, and compare the color with that of standard solutions similarly prepared. If the  $\text{Al}_2\text{O}_3$  content is greater than 0.001 per cent, sodium acetate need not be used.

**Determination of chromium, tin, and molybdenum.** Chromium, tin, and molybdenum can be determined colorimetrically by a method similar to that described above for aluminum.<sup>12,15</sup>

**Detection of ammonia.** When a drop of a solution of hematoxylin is exposed to ammonia gas, an intense carmine-red color appears. This reaction is capable of detecting 1 $\gamma$  of ammonia at a dilution of 1:7,500,000. Potassium, copper, ferrous iron, tin, and lead give similar reactions.<sup>1,8,28,27</sup>

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### HOFFMAN VIOLET 3R

**Use:** Detection of antimony, mercury and tin.

The dye (Color Index, 679) is a mixture of methylated or ethylated rosaniline and pararosaniline of varying composition. It is a green crystalline powder, soluble in water with a magenta solution. It is insoluble in alcohol, and soluble in sulfuric acid with a yellowish-brown color. For the method of preparation, see original reference.<sup>1</sup>

**Detection of mercury, antimony and tin.** Smith and Rogers<sup>2</sup> have investigated the possibilities of this dye as an analytical reagent for various cations, and have found that reasonably satisfactory results may be obtained with mercurous mercury, antimony, and stannous tin.

**Procedure.** To 5 ml. of an aqueous solution containing 10 mg. of mercurous ion per ml., add a few drops of an aqueous solution of the dye, and then precipitate with 1 N sulfuric acid. A gray precipitate forms with mercurous mercury.

Antimony is detected as follows:

**Procedure.** To 5 ml. of an hydrochloric acid solution containing an antimony salt, add a few drops of an aqueous solution of the dye, and then precipitate with 5 N ammonium hydroxide. A pale blue precipitate is formed with antimony.

Tin is detected by the following procedure:

**Procedure.** To 5 ml. of an hydrochloric acid solution of a stannous salt, add a few drops of an aqueous solution of the dye, and then precipitate with 5 N ammonium hydroxide. A light blue precipitate forms with stannous tin.

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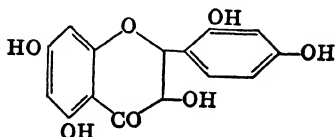
**MORIN**

Synonym: 3,5,7,2',4'-Pentahydroxyflavone

 $C_{15}H_{10}O_7 \cdot 2H_2O$ 

Mol. Wt. 238.26

Beil. Ref. XVIII, 239(423).



**Use:** Detection of aluminum, antimony, arsenic, beryllium, cadmium, calcium, gallium, indium, lead, molybdenum, scandium, strontium, thorium, tungsten, zinc and zirconium.

Determination of aluminum, beryllium, fluoride, and scandium.

Morin is the coloring matter from the wood of *chlorophora tinctoria* (old fustic). It is obtained as pale yellow needles. It melts at  $285^{\circ}\text{C}$ . It is insoluble in water, slightly soluble in ether and acetic acid, and soluble in alcohol and alkalies.

**Detection of aluminum.** In 1867 Goppelsroeder<sup>1,21</sup> called attention to the fact that morin contained in fustic caused a green fluorescence when added to a solution containing an aluminum salt, and he observed that this reaction could be made as a test for very small quantities of aluminum. Schantl<sup>2</sup> has studied this reaction and has presented evidence that the greenish fluorescence appears to be due to the formation of a neutral, colloiddally dispersed aluminum salt,  $Al(C_{15}H_9O_7)_3$ .

This reaction has been studied by many investigators,<sup>2,3,23-26</sup> and is now recommended as one of the more satisfactory methods for detecting aluminum.

Feigl<sup>3</sup> has described the following sensitive spot test for aluminum:

**Procedure.** Treat the solution to be tested with an excess of 2 N potassium hydroxide to precipitate other metals which give a color reaction with morin, and place a drop of the filtrate in the depression of a black spot plate. Acidify with 2 N acetic acid, and add 1 drop of a saturated solution of morin in methyl alcohol. A greenish fluorescence appears if aluminum is present. Better results are obtained with small quantities of aluminum by comparing with a blank. By means of this test 0.2 $\gamma$  of aluminum can be detected at a dilution of 1:250,000.

Shantl<sup>2</sup> was able to identify only 0.0001 $\gamma$  of aluminum by using an arc light and the luminoscope of Tswett.<sup>3</sup> Beryllium, zinc, gallium and scandium salts also yield fluorescent compounds with morin.

A more sensitive procedure is proposed by Feigl:<sup>3</sup>

**Procedure.** Impregnate a strip of filter paper with a freshly prepared alcoholic solution of morin and then allow to dry. Add to this a drop of a neutral or slightly acid solution to be tested, and again dry. Then add 2 or 3 drops of 2 N hydrochloric acid. A spot showing a light green fluorescence under

a quartz lamp indicates the presence of aluminum. By this method 0.005 $\gamma$  of aluminum can be detected at a concentration limit of 1:10,000,000.

If other elements of the ammonium sulfide group are present, it is necessary to remove the morin compounds of these elements with several more drops of dilute hydrochloric acid.

According to Kocsis<sup>4</sup> the morin test will detect as little as 0.001 $\gamma$  of aluminum if the reaction mixture is examined under ultra-violet light.

**Determination of aluminum.** White and Lowe<sup>5</sup> and Goto<sup>6,19</sup> have studied the aluminum-morin reaction, and have found that aluminum can be determined with a high degree of accuracy in concentrations ranging from 0.1 to 1.2 mg. of aluminum per liter by means of the fluorescence of the aluminum salt. The method requires the use of a source of ultra-violet radiation for producing the fluorescence, which is then measured with either a visual or a photoelectric photometer. A calibration curve is first determined and then the analysis of an unknown is accomplished very quickly. The following procedure is recommended:

**Procedure.** Dilute a 25-ml. aliquot of the unknown solution to slightly less than 250 ml., and adjust the pH to 3.3 by means of acetic acid. Then dilute to exactly 250 ml. Place 5 ml. of this solution in a 100-ml. graduated flask, and add 20 ml. of water, and then add 2 ml. of a saturated solution of morin in 95 per cent alcohol and 35 ml. of 95 per cent ethyl alcohol, and dilute to 100 ml. Place this solution in the cell of the photoelectric apparatus and add the morin reagent in 1-ml. portions until the microammeter reading reaches a maximum and then decreases. Then place a second 5-ml. portion of the solution in a second graduated flask, add 20 ml. of water, and then add a quantity of the morin solution which showed the maximum microammeter reading. Add 35 ml. of alcohol, and dilute with water to 100 ml. Allow this mixture to stand for 15 minutes and adjust the temperature to that which was used in constructing the calibration curve, and then measure in a photometer. Calculate the quantity of aluminum present by reference to the calibration curve obtained under similar conditions.

Phosphate, arsenate and fluoride interfere by causing a decrease in the fluorescence. Sulfate in excess of 9 mg. per 100 ml. interferes. Chloride and nitrite do not interfere. Gallium, indium, beryllium and the rare earths give a fluorescence similar to that of aluminum. Lead, zinc and molybdenum also cause a fluorescence if the solution is not sufficiently acid with acetic acid. Silver destroys the fluorescence. Iron and chromium form black precipitates with morin and must be removed. Highly colored ions, such as copper, nickel and cobalt, produce variations in the color. Interfering metals, however, may easily be removed by successive treatment with hydrogen sulfide, sodium peroxide, and ammonium hydroxide. The acidity may be adjusted to the proper value after the removal of interfering ions by neutralizing the solution with 0.1 M sodium hydroxide or acetic acid to an end-point with phenolphthalein and then adding 10 ml. of 0.1 M acetic acid in excess.

The above procedure is more accurate at low concentrations than the well-known method employing aluminon. Alizarinsulfonic acid is more sensitive than

morin, and hematoxlin is not effected by the presence of fluorides. Schams<sup>20</sup> has used morin for the determination of aluminum in plants.

The addition of morin to a solution of an aluminum salt causes a luminescence under ultra-violet light, but the complex fluoride is formed upon the addition of an alkali fluoride and the fluorescence disappears. Okac<sup>7</sup> has used this reaction for the basis for a titrimetric determination of aluminum or fluoride. The titration is carried out in a chamber illuminated by ultra-violet light with morin used as the indicator. The titration is more successful when the aluminum solution is titrated with an alkali fluoride, since the end-point is not easily distinguished when the titration is carried out with the solution of the aluminum salt. Excellent results are claimed for this method, but the conditions of the determination must be faithfully fulfilled, since slight changes in the procedure introduce important changes in the results.

**Detection of beryllium.** Zermatten<sup>8</sup> first observed that morin gives a yellowish-green fluorescence with solutions of beryllium salts containing sodium or potassium hydroxide, and upon the basis of this behavior he proposed a spot test for beryllium in minerals and rocks. Miller<sup>9</sup> has used morin for the detection of beryllium in a systematic scheme of analysis. Venturello<sup>30</sup> has also used this reaction for the detection of beryllium. Sandell<sup>10</sup> has studied this reaction and reports that in a 0.01 or 0.1 N sodium hydroxide solution the sensitivity of the test is 0.01 p.p.m. of beryllium. The test proposed by Sandell is carried out as follows:

**Procedure.** To 10 ml. of the solution to be tested, which is 0.01-0.1 N in sodium hydroxide, add 0.1 ml. of a morin solution prepared by dissolving 0.02 g. of morin in 100 ml. of acetone. This solution is placed in a vial (2 × 7 cm.) and viewed axially in strong daylight against a dark shaded background. The test can be made more sensitive by comparing with a blank solution using distilled water.

The sensitivity of this reaction is greatly increased if the test solution is examined under ultra-violet light. Under these conditions as little as 0.001 p.p.m. of beryllium can be detected in a 0.01 N solution of sodium hydroxide.

Morin alone shows a faint yellowish-brown fluorescence in ultra-violet light, and this limits the sensitivity of the beryllium test. Since 1 or 2 ml. of solution is sufficient for the test, the amount of beryllium detectable is approximately 0.001γ. The sensitivity of the beryllium test decreases with increasing alkalinity of the solution.

Solutions containing sodium, potassium, rubidium, cesium, magnesium, strontium, barium, cadmium, mercury, lanthanum, aluminum, gallium, indium, monovalent thallium, titanium, zirconium, trivalent cerium, thorium, bivalent tin, lead, pentavalent vanadium, arsenic, antimony, bismuth, trivalent chromium, hexavalent molybdenum, tungsten, uranium, trivalent iron, cobalt, nickel, bivalent palladium, and platinum give no color reactions when solutions of their salts are made 0.5-1 N in sodium hydroxide, filtered and the filtrate treated with morin. Columbium and tantalum give no reaction when the oxides are fused with sodium hydroxide and the filtered aqueous extract is tested with morin. Bivalent copper,

silver, gold, and manganese oxidize morin in sodium hydroxide solution and therefore destroy the reagent. Chromates also interfere, probably through oxidation of the reagent. Lithium, calcium, zinc and scandium give a fluorescence similar to that of beryllium when treated with morin in an alkaline solution. The fluorescence with calcium and lithium under the conditions of the test are not perceptible in daylight. The fluorescence given by zinc may be observed in daylight, but this fluorescence is destroyed by the addition of a soluble cyanide. Scandium hydroxide is sufficiently soluble that the filtrate from the precipitated hydroxide contains enough of the element to yield a very faint fluorescence in daylight. This interference, however, can be eliminated by adding a cobalt salt to the scandium solution and precipitating the cobalt and scandium hydroxides simultaneously. The filtrate from yttrium also shows a very faint fluorescence with morin.

Interference due to small quantities of calcium is eliminated by the addition of sodium pyrophosphate. The morin test for beryllium is particularly suitable for the detection of beryllium in the presence of aluminum. One part of beryllium may readily be detected in the presence of 100,000 parts of aluminum by the above procedure. In ultra-violet light, 1 part of beryllium can be detected in 2,000,000 parts of solution.

**Determination of beryllium.** According to Goto<sup>11,6</sup> the intensity of the fluorescence produced when morin is added to a solution of aluminum salt in dilute sodium hydroxide is proportional to the quantity of beryllium present. Consequently, beryllium can be determined colorimetrically by measuring the intensity of the fluorescence of the beryllium compound.<sup>27</sup>

Interference with this reaction is the same as that discussed in the preceding section on the detection of beryllium.

The intensity of the fluorescence caused by beryllium depends upon the concentration of sodium hydroxide, and consequently the alkalinity must be carefully controlled. The intensity of the fluorescence decreases on standing.

The following method is used for the determination of beryllium in a solution free from metals precipitated by an excess of sodium hydroxide. Lithium in appreciable quantities must be absent, and calcium should not be present in concentrations exceeding 1 part in 10,000 parts of solution.

**Reagents.** *Morin solution:* Use a 0.02 per cent solution in ethyl alcohol or acetone.

*Standard beryllium solution:* Dissolve 0.0246 g. of  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$  (tested purity) in water, add 1.0 ml. of concentrated hydrochloric acid, and dilute to 250 ml. with water. This gives a 0.00050 per cent solution.

**Procedure.** Transfer 5 ml. of the sample solution, containing 0.1-8 $\gamma$  of beryllium to a 2  $\times$  7 cm. flat-bottomed vial or tube. Add 2.0 ml. of a saturated aqueous solution of sodium pyrophosphate, and sufficient 1 or 2 N sodium hydroxide to make its concentration about 0.1 M if metals not precipitated with the base are present. If aluminum, lead, or other amphoteric metals are present, add sufficient sodium hydroxide to dissolve completely the precipitate first formed.

If zinc is present, add 1-2 ml. of 5 per cent potassium cyanide (sufficient for a few milligrams of zinc). Then add 0.10 ml. of the morin solution. Prepare in a similar manner a series of standards having the same volume and the same concentration of sodium hydroxide as the unknown. Compare in ultra-violet light. Hold the tubes or vials vertically above the lamp, and view transversely.

The comparison may be made in strong daylight against a dark shaded background if the quantity of beryllium exceeds  $0.5\gamma$ . When the determination is carried out in this way, use 0.5 ml. of the morin solution. The solution should not be exposed too long to sunlight.

**Detection of gallium.** Like aluminum, gallium also yields a greenish-fluorescence in a neutral or slightly acetic acid solution when treated with morin. According to Beck<sup>12,13</sup> this reaction is even more sensitive than that for aluminum. The fluorescence caused by aluminum disappears when the solution is treated with sodium fluoride, but the effect of sodium fluoride on the fluorescence caused by gallium is much less pronounced. In this way gallium and aluminum may be differentiated from one another.

The test is carried out by treating a neutral or slightly acetic acid solution to be tested with a 5 per cent alcoholic solution of morin. By carrying out the reaction on filter paper,  $0.1\gamma$  of gallium can be detected at a concentration of 1:300,000. By using a volume of 5 ml. of solution in a test tube the reaction serves to detect  $0.85\gamma$  of gallium at a dilution of 1:6,000,000. Under ultra-violet light  $0.015\gamma$  of gallium can be detected at a concentration of 1:300,000,000.

Wenger and Duckert<sup>14</sup> have studied the various methods which have been proposed for the detection of gallium, and recommend the procedure of Beck.<sup>12,13</sup>

**Detection of scandium.** Morin reacts with scandium salts to give a compound which possesses a green fluorescence, even in daylight. Under ultra-violet light as little as  $0.03\gamma$  of scandium is sufficient to give a test, which probably depends upon the formation of a colloidal solution of the scandium salt of morin. The fluorescence is extinguished by the addition of an alkali fluoride.<sup>13,15</sup>

**Determination of scandium.** The formation of the fluorescent complex of scandium with morin in a neutral or faintly acid solution provides a useful method for the determination of scandium in the absence of aluminum, beryllium, gallium, and other metals which react similarly. Certain salts or compounds of scandium with organic acids can be extracted from aqueous solution by means of such organic solvents as butyl alcohol, amyl alcohol, and ethyl acetate. The addition of an alcoholic solution of morin to the organic solvent phase produces a greenish fluorescence. Although this extraction does not provide a means of separating scandium from interfering substances, it does make possible an increase in the sensitivity of the morin reaction for scandium. Best results are obtained by extracting as the benzoate. Aluminum, beryllium, gallium, and indium cause fluorescence in the organic phase. Ferric iron in the organic phase does not produce a fluorescence with morin, but interferes with the scandium reaction by absorbing ultra-violet radiation. The extraction of scandium is best carried out in a neutral or very faintly acid solution. Ammonium acetate is used

to buffer the solution to pH 7. The sample and comparison solutions should have very nearly the same pH, since a difference of more than 0.2 pH unit may cause a large error.

Johnsen<sup>28</sup> has studied the scandium determination, and gives the following method, which is described by Sandell.<sup>29</sup>

**Reagents.** *Morin solution:* Prepare a 0.01 per cent solution of morin in alcohol or acetone.

*Ammonium acetate solution:* Dissolve 50 g. of ammonium acetate in 100 ml. of water.

*Sodium benzoate:* Dissolve 25 g. of sodium benzoate in 100 ml. of water.

*Standard scandium solution:* Prepare a 0.001 per cent solution of scandium in 0.1 N sulfuric acid.

**Procedure.** For the determination, use 5-15 ml. of solution containing 0.2-5 $\gamma$  of scandium. If the unknown solution is acid, make approximately neutral by adding aluminum-free sodium hydroxide. Transfer the sample and a suitable standard to separate 25-ml. glass-stoppered tubes, and treat as follows: Add 2.0 ml. of the ammonium acetate solution and 1.0 ml. of the sodium benzoate solution. Mix thoroughly, and add 2.0 ml. of ethyl acetate. Use 3-4 ml. of ethyl acetate for quantities of scandium approximating 5 $\gamma$ . Shake well and allow to stand until the phases separate. Add 0.05 ml. of the morin solution to the upper layer, and mix by agitating gently. Compare the fluorescence of the upper layers of the standard and unknown tubes in ultra-violet light.

**Detection of indium.** Indium, like aluminum, scandium and gallium, gives an intense green fluorescence with morin. The fluorescence is most intense in solutions containing a little mineral acid. It is observable even in daylight. The fluorescence is weakened by addition of sodium acetate and soluble fluorides, but not to the same extent as with gallium.<sup>13</sup>

Although the elements aluminum, scandium, gallium and indium show almost the same fluorescence with morin, it is possible to detect these four elements in the presence of one another. The slightly acid solution to be tested is treated with an alcoholic solution of morin. A fluorescence is produced if 1 $\gamma$  of any one of the elements is present. The addition of sodium fluoride causes the disappearance of the fluorescence due to aluminum or scandium. A second portion of the acid solution is treated with an excess of ammonium carbonate. Morin shows a fluorescence only with scandium under these conditions. On the other hand, the fluorescence due to scandium disappears upon the addition of an ammoniacal tartrate solution, but this treatment has no effect upon the fluorescence due to aluminum. If, after the addition of sodium fluoride, the fluorescence persists, the addition of hydrogen sulfide precipitates indium as indium sulfide, and its fluorescence disappears, whereas gallium gives a fluorescence in the filtrate.<sup>13</sup>

**Detection of thorium.** Beck and Goto<sup>11,16</sup> have recommended the use of morin for the detection of thorium, but Wenger and Duckert,<sup>17</sup> who have studied

various methods used for the detection of this element, claim that the test is too general and resembles the reactions of other metals of the same group.

**Detection of antimony.** In the presence of hydrochloric acid, trivalent antimony gives a strong yellowish-green fluorescence with morin. This reaction can be used to detect 0.05 $\gamma$  of antimony.<sup>6,18</sup>

**Fluorescence analysis.** Goto<sup>11,16,18</sup> has studied the reaction of a number of ions with morin and reports that this reagent can be used for the detection of lead, cadmium, zinc, strontium, calcium, zirconium, tungsten, molybdenum, arsenate and arsenite. All of these ions give a yellowish-green fluorescence. The sensitivity of these reactions are given in Table 54.

TABLE 54.—FLUORESCENCE REACTIONS WITH MORIN

Ion	Sensitivity in $\gamma$
Lead	0.25
Cadmium	0.1
Zinc	0.05
Zirconium	2.5
Tungsten	0.25
Molybdenum	0.5
Arsenite	Not sensitive

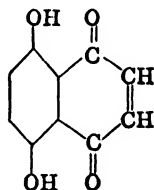
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**NAPHTHAZARIN**Synonym: 5,8-Dihydroxy- $\alpha$ -naphthoquinone $C_{10}H_6O_4$ 

Mol. Wt. 190.15

Beil. Ref. VIII, 412.

**Use:** Detection of aluminum, beryllium and magnesium.

Naphthazarin is obtained as brownish-red needles with a golden luster when purified by sublimation. It is obtained as brown needles with a greenish luster when crystallized from alcohol. The compound is slightly soluble in ether and boiling water, and is moderately soluble in alcohol to which it imparts a red color. It is somewhat more soluble in acetic acid. It dissolves in solutions of alkalis with the formation of a corn-flower blue solution.

**Preparation:** Place 400 g. of concentrated sulfuric acid and 40 g. of fuming acid in a 2-liter porcelain dish and heat on a sand-bath to 200° C. Add in 5-g. portions 40 g. of dinitronaphthalene, alternately with small portions of zinc until 10-15 g. of the latter has been added. The temperature of the reaction mixture should not exceed 200° C., and should not fall below 195° C. The reaction is complete when a test portion of the solution dissolves in water with the appearance of a violet color. At this point, filter, cool, and separate the slimy precipitate. Boil with 1600 ml. of water, and filter hot through a fluted filter. The dye separates from the filtrate as a jelly-like mass. Wash well, dry, and sublime in a large porcelain dish. A part of the material chars during this treatment.<sup>1,2</sup>

**Detection of magnesium and aluminum.** Hahn, Wolf, and Jäger<sup>3</sup> assumed that the color principle of the alkanna root, which has been used for the detection of magnesium, was a hydroxy derivative of anthraquinone; but Raudnitz,<sup>4,5</sup> Dieterle and co-workers<sup>6</sup> and Betrabet and Chakravarti,<sup>7</sup> have shown that alkanin is a derivative of naphthazarin.

Dubsky and Wagner<sup>8</sup> have shown that naphthazarin can be used for the detection of aluminum and magnesium in the same manner as alkanin. If the



tests are carried out in a cold solution which has been made alkaline with sodium hydroxide, the sensitivity of the reaction is only 0.5-1.0 mg. of magnesium. If, however, ethylenediamine is used in place of sodium hydroxide for the precipitation of the aluminum or magnesium hydroxide, and the mixture is warmed slightly, the test is one thousand times more sensitive. The following procedure for detecting magnesium is recommended:

**Procedure.** To a few drops of the solution to be tested, add a few drops of a mixture of 5 ml. of 0.03 per cent naphthazarin solution and 1 ml. of 10 per cent ethylenediamine solution. A blue color is obtained with magnesium. The sensitiveness of this reaction is 1:66,000.

This test may also be applied as follows:

**Procedure.** To 50 ml. of the solution to be tested, add 5 drops of 0.03 per cent naphthazarin solution, and then add dropwise a slight excess of 2.5 N sodium hydroxide solution. A blue precipitate forms at once or on warming if magnesium is present.

To detect aluminum proceed as follows:

**Procedure.** To 5 ml. of the solution to be tested, add 2 ml. of 0.03 per cent naphthazarin solution, and then add with stirring sufficient ammonia to change the color from dark red to blue, and then add an additional 3 ml. of ammonia. A dark violet precipitate is obtained if aluminum is present. The test for aluminum in an ammoniacal solution fails when less than 0.05 mg. of aluminum is present.

**Detection of beryllium.** Dubsky and Krametz<sup>9</sup> have used naphthazarin for the detection of small quantities of beryllium.

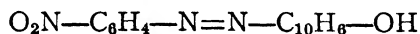
**Procedure.** Mix 30 drops of a 0.03 per cent naphthazarin solution with 5 drops of 10 per cent ethylenediamine solution. Dilute with water until the dirty, bluish-violet color changes to a pure blue. If a solution containing a beryllium salt is added, the color changes to a reddish-violet. This reaction is sensitive to 1.2 $\gamma$  of beryllium.

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**p-NITROBENZENEAZO- $\alpha$ -NAPHTHOL** $C_{16}H_{11}O_3N_3$ 

Mol. Wt. 293.27

Beil. Ref. XVI, 155(268).

**Use:** Detection of magnesium. ·

*p*-Nitrobenzeneazo- $\alpha$ -naphthol occurs as a bright red powder which shows a fluorescence in an alkaline solution.

**Preparation:** Diazotize a solution of 0.6 g. *p*-nitroaniline in hydrochloric acid in the usual manner, and couple with a solution of 0.5 g. of  $\alpha$ -naphthol in an alkaline solution. The violet color of the alkali salt of *p*-nitrobenzeneazo- $\alpha$ -naphthol indicates that the coupling has taken place. Precipitate the dye by acidifying with hydrochloric acid, filter with suction, wash with dilute hydrochloric acid, and finally with water until free from acid. Allow to dry. The bright red powder which is obtained is unsuitable for recrystallization.<sup>1</sup>

The  $\beta$ -isomer is removed by boiling 10 g. of the impure product twice with 140 g. of amyl alcohol.<sup>1</sup>

**Detection of magnesium.** Many of the tests which have been proposed for magnesium depend upon the adsorption of organic dyes upon precipitated magnesium hydroxide. Certain dyes of the azo and anthraquinone series undergo a change in color upon adsorption on magnesium hydroxide; and, since the adsorption of the dye is instantaneous, the resulting color change affords an excellent test for magnesium. *p*-Nitrobenzeneazo- $\alpha$ -naphthol appears to be particularly suitable for this purpose. A solution of the reagent in an alkaline medium is red to red-violet in color, but this is changed to a deep blue upon being adsorbed by magnesium hydroxide which is formed when the alkaline reagent is added to a solution of a magnesium salt. The coloration of the precipitate appears to be due to the adsorption of the alkali salt of the dye, since the pure dye in an alcohol or chloroform solution is adsorbed by magnesium hydroxide without a change in color, and the color then changes immediately when an alkali is added. The test is much more sensitive if sodium hydroxide rather than ammonium hydroxide is used in making the test.

The magnesium test is best carried out so that the precipitation and coloration of the hydroxide occur simultaneously. This may be accomplished by using an alkaline solution of the dye as the test reagent.

**Reagent.** Dissolve 0.001 g. of *p*-nitrobenzeneazo- $\alpha$ -naphthol in 100 ml. of N sodium hydroxide solution.

**Procedure.** Place a drop of the solution to be tested upon a spot plate and add 1-2 drops of the reagent. A blue precipitate or a color change from red-violet to blue occurs in the presence of magnesium. In making the test it is necessary that an excess of the alkali is present, since if the solution is acid after the addition of the reagent, the yellow color of the free dye appears. In

this case add a few drops of sodium hydroxide solution. The test is made more sensitive by comparing with a blank formed from distilled water.

By means of this test as little as 0.025 mg. of magnesium can be detected by means of a blue precipitate. With smaller quantities of magnesium, a blue coloration appears due to the formation of a colloidal suspension of magnesium hydroxide particles.

The sensitivity of this test is 0.19% of magnesium at a dilution of 1:260,000.

It is important to note that the violet, alkaline solution of *p*-nitrobenzeneazo- $\alpha$ -naphthol is adsorbed with the formation of a blue color by pure filter paper which is free of magnesium. Consequently, the spot test for magnesium cannot be carried out upon filter paper, but only upon a spot plate. Calcium hydroxide and calcium carbonate are also colored by *p*-nitrobenzeneazo- $\alpha$ -naphthol and must be absent in making the test.

Ions which are capable of forming hydroxides which either adsorb the dye with color formation, or which are themselves colored, also interfere with the test for magnesium. Further, substances such as aluminates, zincates and stannates, which are soluble in the alkaline solution, may prevent, in part at least, the adsorption of the dye. The alkaline earth hydroxides and bismuth hydroxide also interfere by making the observation of the color change difficult. The interference by those metals which form complex cyanide ions, such as nickel, cobalt, copper, silver, cadmium, and zinc may be partially eliminated by the addition of a large excess of potassium cyanide to the test drop on the spot plate. Lead, which forms a soluble plumbite with sodium hydroxide, is without serious effect upon the test, and magnesium can be detected in the presence of comparatively large quantities of lead.

If iron, trivalent chromium, aluminum and tin are present, the following procedure must be used:

**Procedure.** Place 2 drops of the solution to be tested in a small test tube and add a few crystals of sodium nitrite, and heat for a time over a boiling water-bath. By this treatment iron, chromium and tin are precipitated as the hydroxides. Centrifuge the mixture and transfer the supernatant liquid to a spot plate and carry out the test as described above.

Chromates affect the magnesium test only slightly, although the solution may be rather highly colored.

Interference due to manganese may be eliminated by treating the solution to be tested with a little colorless ammonium sulfide, centrifuging, and applying the test to the clear supernatant liquid. The dye is reduced after a short time by an excess of ammonium sulfide to form a red amino-azo dye, and consequently it is essential to carry out a blank test. In this way 13% of magnesium can be detected in the presence of 500 times as much manganese.

If calcium is present in the solution to be tested for magnesium, use the following procedure:

**Procedure.** Place a drop of the solution to be tested on a spot plate, acidify slightly, and treat with 1-2 drops of a slightly alkaline solution of *p*-nitrobenzeneazo- $\alpha$ -naphthol. Then add a dilute solution of sodium hydroxide drop-

wise until a slight precipitate of calcium hydroxide appears. If the solution appears blue when compared with the blank test under exactly similar conditions on a pure calcium solution, then magnesium is present. The calcium hydroxide precipitate is colored blue only when a large excess of sodium hydroxide is present.

Strontium and barium hydroxides, unlike calcium hydroxide, are not colored blue by the dye. A large excess of alkali should be avoided, however, in the precipitation of magnesium, since a precipitate of strontium or barium might mask the magnesium test.

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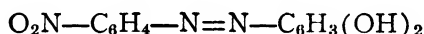
### ***p*-NITROBENZENEAZORESORCINOL**

Synonym: *o,p*-Dihydroxy benzeneazo-*p'*-nitrobenzene

$C_{12}H_9O_4N_3$

Mol. Wt. 259.22

Beil. Ref. XVI, 181.



**Use:** Detection of cobalt, magnesium, nickel and zinc.

This compound is obtained as a dark red crystalline powder from alcohol. It melts at 199-200° C. It is almost insoluble in boiling alcohol, acetic acid, and toluene. It is soluble in solutions of alkalis with the formation of a violet solution.

**Preparation:** Diazotize 1.4 g. of *p*-nitroaniline in the usual manner, and add gradually to a solution containing 1.1 g. of resorcinol dissolved in dilute sodium hydroxide solution. Acidify and collect the reddish-brown precipitate, wash and dry.

**Detection of magnesium.** Suitsu and Okuma<sup>1</sup> first proposed the use of this reagent for the detection of small quantities of magnesium. The dye dissolves in alkalis to form bluish-violet solutions, but in the presence of a magnesium salt a sky blue precipitate forms. This precipitate is not a compound of magnesium nor a lake, but it is the result of the adsorption of the dye on precipitated magnesium hydroxide.<sup>2</sup> The test is carried out as follows:<sup>3</sup>

**Procedure.** Evaporate the solution to be tested to dryness in a porcelain dish, and then add 5-10 ml. of 6 N sodium hydroxide and 1 drop of 0.5 per cent solution of the dye in 1 per cent sodium hydroxide. Allow to stand at least 10 seconds. A blue stain which turns green when washed with water, and which is not affected by ammonium hydroxide indicates the presence of magnesium.

This test is less sensitive in the presence of salts of tartaric acid, acetic acid, and ammonium hydroxide. The sensitiveness is about 0.003 mg. of magnesium.

A spot reaction has been proposed by Stone.<sup>4</sup>

**Procedure.** Immerse filter paper in a 0.01 per cent alcoholic solution of the reagent and dry. Cut the paper into squares for use. To make the test, place a drop of the solution to be tested on the prepared paper, dry, and immerse in a 1 per cent solution of sodium hydroxide. Magnesium gives a blue spot on a reddish field. If the original solution contains much acid, the spot is yellow at first. As little as 0.005 mg. of magnesium gives the test.

This reaction is not specific for magnesium, since interference may arise from the formation of colored hydroxides, or from hydroxides which adsorb the dye to give a colored product. For example, nickel salts give an almost identical reaction, and cobalt salts give a similar color. Beryllium, lanthanum, zinc, cadmium, and aluminium may interfere.<sup>5</sup> Aluminates, zincates, and stannates may prevent the adsorption of the dye on the magnesium hydroxide. Barium, strontium, and calcium, which are so troublesome in detecting magnesium by precipitation as magnesium ammonium phosphate, do not interfere.<sup>6</sup> Arsenates, chromates, and permanganates may interfere, but most common anions do not. The test is less sensitive in the presence of tartrates, acetates, and ammonium salts.<sup>6</sup> Further, the sensitivity of the test is materially reduced when large quantities of hydroxides are formed, even though the latter are colorless and do not adsorb the dye, since their formation in an alkaline solution makes it difficult or impossible to detect the color of the magnesium reaction. The reaction generally seems to be reliable only in the absence of ammonium salts and all ions except arsenite, beryllium, cerous compounds, lithium, sodium, silver, strontium, thallium, acetate, chloride, permanganate, nitrate, nitrite, sulfate, and vanadate.<sup>14</sup>

This reaction has been used extensively for the detection of magnesium.<sup>7-12, 15-19</sup>

**Detection of zinc.** Wenger and others<sup>13</sup> recommend *p*-nitrobenzene-azoresorcinol for the detection of zinc. A 0.025 per cent solution of the reagent in *N* sodium hydroxide gives a spot reaction with as little as 0.05 $\gamma$  of zinc. Beryllium and magnesium give similar tests.

**Determination of cobalt and nickel.** *p*-Nitrobenzeneazoresorcinol yields a blue color with cobalt and nickel, and can be used to detect these metals.<sup>5</sup> The sensitivity of these reactions is 1:100,000.

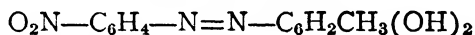
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**p-NITROBENZENEAZOORCINOL**    Synonym: *p*-Nitrophenylazoorcinol

$C_{18}H_{11}O_4N_3$

Mol. Wt. 273.24



**Use:** Detection of beryllium and zinc.

*p*-Nitrobenzeneazoorcinol is a dark reddish-brown powder. It dissolves in sodium hydroxide solution with a formation of a yellow color.

**Preparation:** Dissolve 1.38 g. of *p*-nitroaniline in dilute hydrochloric acid, cool to 0° C., and add a solution of 0.85 g. of potassium nitrite dissolved in water, which is also cooled to 0° C. Still keeping the temperature at 0° C., mix the resulting solution of *p*-nitrobenzenediazonium chloride with a cold solution containing 1.42 g. of orcinol that has been made alkaline with sodium carbonate. Acidify the mixture, filter off the bright red crystals which form, wash with dilute hydrochloric acid and then water, and dry.<sup>1</sup>

**Detection of beryllium and zinc.** The yellow alkaline solution of *p*-nitrobenzeneazoorcinol forms an orange-red lake with solutions of beryllium salts, and in this respect behaves somewhat like quinalizarin. This reaction has been used by Komarovskii and Poluektov<sup>1</sup> for the detection of small quantities of beryllium.

**Reagent.** Dissolve 25 mg. of *p*-nitrobenzeneazoorcinol in 100 ml. of N sodium hydroxide.

**Procedure.** Place a drop of the reagent on a strip of filter paper, and apply to the middle of the yellow area a very small drop of the solution to be tested by means of a capillary tube. Then add a second drop of the reagent. If beryllium is present, an orange-red color appears. If small quantities of beryllium are present, only the center of the drop is colored orange-red, but with larger concentrations, the entire spot may be colored. As little as 0.2γ of beryllium in 0.04 ml. of solution can be detected.

Magnesium salts react with alkaline solutions of the dye to yield a brown-yellow precipitate. Zinc hydroxide gives a color reaction similar to that of

beryllium hydroxide, but the color disappears on the addition of potassium cyanide, due to the formation of the soluble complex,  $K_2[Zn(CN)_4]$ . The addition of potassium cyanide is of further value, since it prevents the precipitation of hydroxides of nickel, copper, cobalt, cadmium and silver. Aluminum, alkaline earths and the salts and hydroxides of the rare earths do not interfere with this reaction.

Kulcsar<sup>4</sup> has used the reaction of beryllium with *p*-nitrobenzeneazoorcinol for the detection of beryllium in copper-base alloys, and for the detection of beryllium in the field analysis of ores.

**Determination of beryllium.** The color of a solution of *p*-nitrobenzeneazoorcinol in 0.1 N sodium hydroxide is changed at a suitable pH from bright yellow to reddish-brown by the  $BeO_2^{-2}$  ion. This change cannot be evaluated visually, but the color can be measured photometrically. The following method is used for the determination of beryllium in aluminum and aluminum alloys:<sup>3</sup>

**Reagent.** Stir 0.25 g. of *p*-nitrobenzeneazoorcinol for several hours with 100 ml. of 0.1 N sodium hydroxide solution.

**Procedure.** Place 0.1-0.6 g. of the metal borings in a centrifuge tube and treat with 0.74 ml. of 5 N sodium hydroxide solution for each 0.1 g. of the sample. Then add 2 ml. in excess. Cool at first, if necessary, but eventually heat in boiling water. Dilute the solution to about 15 ml., centrifuge, and decant into a 50-ml. volumetric flask. Wash the residue with small portions of water, and add the washings to the solution in the flask. Dilute to 50 ml., mix, and use a suitable aliquot. Transfer this with a pipet to a 25-ml. measuring cylinder, and add sufficient 2 N sodium hydroxide to make a total of 6 milliequivalents of sodium hydroxide (this includes the 2 ml. excess used, and that contained in the reagent). Add 5 ml. of 0.64 M boric acid solution, dilute to 19 ml., mix, and add 6 ml. of the reagent solution. Again mix, and measure the extinction.

Excellent results are obtained with alloys containing 0.005-18.0 per cent beryllium.

Osborn and Stross<sup>2,6</sup> have used a similar method for the determination of beryllium in minerals and rocks.

1. A. S. Komarovskii and Poluektov, *Mikrochemie* **14**, 315-17 (1934); *C.A.* **28**, 6387 (1934).
2. C. W. Osborn and W. Stross, *Metallurgia* **30**, 3-6 (1944); *C.A.* **39**, 2940 (1945).
3. W. Stross and G. H. Osborn, *J. Soc. Chem. Ind.* **63**, 249-51 (1944); *C.A.* **39**, 39 (1945).
4. F. Kulcsar, *Chemist-Analyst* **34**, 28, 29, 30 (1945); *C.A.* **39**, 2940 (1945).
5. F. Kulcsar, *Eng. Mining J.* **144**, 103 (1943); *C.A.* **38**, 696 (1944).
6. G. H. Osborn and W. Stross, *Metallurgia* **30**, 3-6 (1944); *C.A.* **39**, 881 (1945).

## PENTAMETHYLQUERCETIN

**Use:** Detection and determination of boron.

**Detection and determination of boron.** The pentamethyl derivative of quercetin (an isomer of morin) yields a yellow color with boric acid. This reaction may be used to detect small quantities of boron. The color does not

obey Beer's law, but by using standards prepared from potassium chromate, it is possible to determine 0.4-1.8 mg. of boric acid with an accuracy of 15 per cent.<sup>1-3</sup>

1. C. W. Wilson, *J. Am. Chem. Soc.* **61**, 2303-06 (1939); *C.A.* **33**, 9201 (1939).
2. S. Rangaswami and T. R. Seshadri, *Proc. Indian Acad. Sci.* **16A**, 129-34 (1942); *C.A.* **37**, 1102 (1943).
3. K. Neelakantam and S. Rangaswami, *Proc. Indian Acad. Sci.* **18A**, 171-8 (1943); *C.A.* **38**, 698 (1944).

## PHENOSAFRANINE

$C_{18}H_{15}N_4Cl$

Mol. Wt. 322.76

Color Index, 840.

**Use:** Detection of antimony, mercury and silver.

**Preparation:** Mix 1 mole of *p*-phenylenediamine hydrochloride with 2 moles of aniline hydrochloride and oxidize with potassium dichromate. Add powdered chalk, filter, and acidify the filtrate with hydrochloric acid, and salt out. The compound crystallizes from dilute hydrochloric acid as green needles.<sup>2</sup>

**Detection of silver, mercury and antimony.** Smith and Rogers<sup>1</sup> have investigated the possibilities of this dye as an analytical reagent for various cations, and have found that reasonably satisfactory results may be obtained with silver, antimony, and mercurous mercury.

**Procedure.** To 5 ml. of silver solution containing 10 mg. of silver per ml., add a few drops of an aqueous solution of the dye, and then precipitate with 4 N sodium carbonate. A pale green precipitate forms with silver ions.

Mercury may be detected by the same procedure as with silver. A dark green precipitate forms with mercurous mercury.

Antimony is detected as follows:

**Procedure.** To 5 ml. of an hydrochloric acid solution of antimony salt, add a few drops of an aqueous solution of the dye, and then precipitate with 5 N ammonium hydroxide. A light purple precipitate forms if the solution contains 10 mg. of antimony per ml.

1. J. W. Smith and H. E. Rogers, *J. Chem. Ed.* **16**, 143-4 (1939); *C.A.* **33**, 3287 (1939).
2. R. Bindschedler, *Ber.* **13**, 207 (1880); **16**, 870 (1883).

## PHLOXINE

$C_{20}H_3O_5Cl_2Br_4Na_2$

Mol. Wt. 759.80

Color Index, 778.

**Use:** Detection of mercury.

**Preparation.** The dye is obtained by brominating dichlorofluorescein, which is prepared by condensing resorcinol and dichlorophthalic acid.<sup>1,2</sup>



**Detection of mercury.** Phloxine is a xanthene dyestuff which has been studied in connection with cation detection. Only mercurous mercury gives any useful color reaction.

**Procedure.** To 5 ml. of an aqueous solution containing 10 mg. of mercurous ion per ml., add a few drops of an aqueous solution of the dye, and then precipitate with 4 N sodium carbonate or 1 N sulfuric acid. With sodium carbonate, the silver solution yields a dark green precipitate, and with sulfuric acid a light pink precipitate.

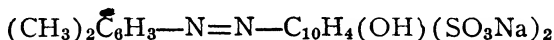
1. C. Graebe, *Ber.* 33, 2019 (1900).
2. C. Graebe and S. Gourevitz, *Ber.* 33, 2023 (1900).
3. J. W. Smith and H. E. Rogers, *J. Chem. Ed.* 16, 143-4 (1939); *C.A.* 33, 3287 (1939).

### PONCEAU 2R

 $C_{18}H_{14}N_2O_7S_2Na_2$ 

Mol. Wt. 480.41

Color Index, 79.



**Use:** Detection of silver.

The dye is a bright red powder. It is insoluble in alcohol, but dissolves readily in water with a yellowish-red solution.

**Preparation:** The dye is prepared by diazotizing *m*-xylidine and coupling the resulting product with pure  $\beta$ -naphthol-3,6-disulfonic acid.<sup>1</sup>

**Detection of silver.** Ponceau 2R may be used as a fairly satisfactory test for the silver ion.<sup>2</sup>

**Procedure.** To 5 ml. of an aqueous solution of a silver salt containing 10 mg. of silver ion per ml. of solution, add a few drops of an aqueous solution of the dye, and then precipitate with 4 N sodium carbonate or 1 N sulfuric acid. A yellow-gray precipitate forms with sodium carbonate and a pink precipitate with sulfuric acid.

1. E. Grandmougin, *J. prakt. Chem.* 76, 128 (1907).
2. J. W. Smith and H. E. Rogers, *J. Chem. Ed.* 16, 143-4 (1939); *C.A.* 33, 3287 (1939).

### PONTOCHROME BLUE BLACK R

Synonym: Chrome Blue N

 $C_{20}H_{13}O_5N_2SNa$ 

Mol. Wt. 416.36

Color Index, 202.



**Use:** Detection of aluminum.

The dye is a dark brown powder. It dissolves in water with a violet solution, and in alcohol with a bluish-red solution. It is also soluble in sodium hydroxide with a Bordeaux-red solution and in sulfuric acid to give a blue color.

**Preparation:** Diazotize  $\alpha$ -naphthylamine-2,4-disulfonic acid, replace the sulfonic acid group in the 2-position by means of sodium hydroxide, and then couple the resulting diazo compound with  $\beta$ -naphthol.

**Detection of aluminum.** When pontochrome blue black R is added to a solution of an aluminum salt, and the resulting mixture is examined under ultra-violet light, an orange-red fluorescence is observed, and this may be used to detect aluminum in the presence of beryllium and many other metals.<sup>1,2</sup>

**Reagent.** Prepare a 0.1 per cent solution of the dye in 95 per cent ethyl alcohol. This reagent appears to be permanently stable.

**Procedure.** Make solution to be tested alkaline with sodium hydroxide and filter. Chromates and fluorides must be removed. Make the solution acid with acetic acid and heat to 80° C., and then add 0.5 ml. of the reagent. If the solution is very dilute allow to stand 30 minutes. An orange-red fluorescence observed under ultra-violet light is a positive test.

The reaction is sensitive at a dilution of 1:5,000,000. With an argon bulb, one part of aluminum in 100,000 parts of water can be detected. Silver, mercury, lead, bismuth, cadmium, arsenic, antimony, tin, zinc, manganese, gallium, indium, thallium, calcium, strontium, barium, magnesium, sodium, potassium, ammonium, lithium, rare earths, chloride, nitrate, sulfate, phosphate and tartrate do not interfere. Colored ions, such as copper, chromium, iron, nickel and cobalt, mask the fluorescence, but after precipitation with sodium hydroxide and acidifying with acetic acid the fluorescence can be observed. Beryllium does not interfere. The test is apparently due to the formation of the aluminum salt of the dye. The intensity of the fluorescence appears to vary with the aluminum content within a limited range.

Pontochrome blue black R possesses the advantage over both morin and aluminon, which are sensitive to small quantities of aluminum, in that beryllium does not interfere.

1. C. E. White and C. S. Lowe, *Ind. Eng. Chem., Anal. Ed.* **9**, 430-1 (1937); *C.A.* **31**, 7787 (1937).
2. M. Bourstyn, *Bull. Soc. Chim.* **8**, 540-1 (1941); *C.A.* **36**, 1563 (1942).

## PYRONIN

$C_{17}H_{19}N_2OCl$

Mol. Wt. 302.78

Color Index, 739.

**Use:** Detection of mercury, silver and tin.

The dye occurs as glistening green crystals, which dissolve in water and alcohol to form red solutions with a yellow fluorescence.

**Preparation:** Dissolve 5.6 g. of dimethyl-*m*-aminophenol in 12 ml. of alcohol, cooled to 0° C., and then add 1.6 ml. of 40 per cent formaldehyde. Filter and crystallize the precipitate from benzene (m.p. 178°). Stir 3 g. of the crystals into 15 g. concentrated sulfuric acid and heat on a water bath 2-3 hours. The reaction

is complete when a sample precipitated with sodium hydroxide and filtered gives no precipitate with acetic acid. Pour the mixture onto 100 g. of ice and nearly neutralize with sodium hydroxide. Add 8 g. concentrated hydrochloric acid and oxidize with a solution of 1.6 g. sodium nitrite in 10 ml. of water. Salt out.<sup>2</sup>

**Detection of silver, mercury and tin.** Pyronin may be used as a fairly satisfactory test for silver, mercury and tin.<sup>1</sup>

**Procedure.** To 5 ml. of a solution of a silver salt containing 10 mg. of silver ion per ml., add a few drops of an aqueous solution of the dye, and then precipitate with 4 N sodium carbonate. A yellow-green precipitate forms with silver.

Using the same procedure, a green precipitate forms with mercurous mercury.

Tin may be detected as follows:

**Procedure.** To 5 ml. of a hydrochloric acid solution of stannous tin, add a few drops of an aqueous solution of the dye, and then precipitate with 5 N ammonium hydroxide. A light blue precipitate forms with solutions containing 10 mg. of stannous ion per ml.

1. J. W. Smith and H. E. Rogers, *J. Chem. Ed.* **16**, 143-4 (1939); *C.A.* **33**, 3287 (1939).
2. R. Möhlau and P. Koch, *Ber.* **27**, 2896 (1894).

## QUERCETIN

Synonym: Meletin, flavin, sophoretin, tetrahydroxyflavanol

$C_{15}H_{10}O_7 \cdot 2H_2O$

Mol. Wt. 338.26

Beil Ref. XVIII, 242.

**Use:** Detection of iron and uranium.

Determination of aluminum.

Quercetin, an isomer of morin, is a yellow, crystalline powder. It melts at 312-314° C. when anhydrous. It is almost insoluble in water, but is soluble in solutions of alkali hydroxides, in 300 parts of absolute alcohol, and 25 parts of boiling absolute alcohol.

**Determination of aluminum.** Davydov and Devekki<sup>1</sup> have studied various methods for the determination of aluminum employing alizarin, pontachrome blue black, and morin, and have found that for one reason or another these substances are generally unsatisfactory. For example, the fluorescent intensity of the reaction between aluminum and alizarin in weakly acid solutions is not sufficient to be utilized for the aluminum determination; the method of White and Lowe (see pontachrome blue black) is unsuited because the reaction proceeds only within narrow pH limits, and also depends on the amount of coloring matter used; and morin is frequently difficult to obtain. Quercetin, however, when used like morin, gives satisfactory results.

**Procedure.** Place not more than 5 ml. of the solution to be analyzed in a 15-ml. nephelometer, and add 2.8 ml. of a buffer solution prepared by mixing

50 ml. of N sodium acetate with 20 ml. of N hydrochloric acid. Add 3.6 ml. of alcohol, 2 ml. of 0.1 per cent quercetin solution, and then dilute with water to 14 ml. Mix and measure in a nephelometer. The aluminum content of the solution is obtained from a calibration curve which is constructed by using standard aluminum solutions treated as above.

The maximum intensity is obtained immediately after the addition of the quercetin. It is stable for several hours.

**Detection of iron and uranium.** Iron and uranium can be detected by a sensitive spot test using an alcoholic solution of quercetin.<sup>2</sup>

**Procedure.** Add a drop of the solution to be tested to a strip of filter paper (Schleicher and Schull, No. 598), and immediately add to the still damp spot, a drop of a 0.2 per cent alcoholic solution of quercetin. In a few seconds an olive-green ring forms with uranium and a rust-brown ring with iron.

By this reaction, 0.3γ of iron and 3.0γ of uranium can be detected. Ferrous and ferric iron cannot be distinguished with this reagent.

1. A. L. Davydov and U. S. Devikki, *Zavodskaya Lab.* 10, 134-8 (1941); *C.A.* 35, 5056 (1941).
2. E. J. Kocsis, *Mikrochemie.* 25, 13-15 (1938); *C.A.* 33, 1623 (1939).

## QUERCETRIN

**Synonym :** Quercimelin, quercetin-rhamnoside, quercitrinic acid

**Use:** Detection of iron and uranium.

Quercetrin ( $C_{21}H_{20}O_{11} \cdot 2H_2O$ ) is a natural product obtained from the bark of *Quercus tinctoria* Bart., Fagaceae, and other plants. It consists of sulfur-yellow, bitter crystals. These melt at 182-185° C. or 250-252° C. when anhydrous. The compound is almost insoluble in water and ether, but it is soluble in alcohol and alkalis.

This reagent is used like quercetin (see above) for the detection of iron and uranium by spot analysis.<sup>1</sup> To make the test, simply substitute quercetrin for quercetin in the above procedure, and proceed exactly as described.

1. E. J. Kocsis, *Mikrochemie*. **25**, 13-15 (1938); *C.A.* **33**, 1623 (1939).

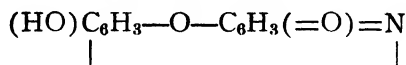
## RESORUFIN

Synonym : 9-Hydroxyisophenoxazone

$$\text{C}_{12}\text{H}_7\text{O}_8\text{N}$$

Mol. Wt. 213.18

Beil. Ref. XXVII, 128.



**Use:** Detection of aluminum, barium, bromine, cadmium, chlorine, chromium, copper, dichromate, hypochlorite, hyposulfite, iron, lead, magnesium, nickel, silver, strontium and zinc.

Resorufin consists of brown needles or dark red prisms. It is insoluble in water and ether and is only slightly soluble in alcohol. It dissolves readily in alkalies to form a carmine-red solution with a vermillion fluorescence.

**Preparation:** Mix 5 g. of resorcinol, 2.5 g. of nitrobenzene and 75 g. of concentrated sulfuric acid, and gradually heat with constant stirring at 170° C. until the melt turns to a violet color. Near the end of the heating period, when the mass begins to thicken, pour into a large quantity of cold water. Neutralize without filtering with sodium carbonate, and evaporate to a small volume. Cool and extract the mixture with alcohol. Distill off the alcohol and precipitate with hydrochloric acid. *p*-Aminophenolsulfonic acid may precipitate with resorufin when the sodium salt is decomposed. To separate, dissolve the precipitate in ammonia, filter, and while hot precipitate with hydrochloric acid. Only resorufin precipitates. Filter with suction, wash with water, and crystallize from hot concentrated hydrochloric acid.<sup>1</sup>

**Detection of metals.** A number of cations can be detected by the precipitates which they form with resorufin: <sup>2,3</sup>

**Reagent.** Dissolve 0.2 g. of resorufin in 5 ml. of ammonium hydroxide and 100 ml. of water.

**Procedure.** Add a few drops of the reagent to a neutral or slightly acid solution containing the metallic salt. Precipitates are obtained with cupric, ferric, chromic, cadmium, aluminum, nickel, zinc, barium and strontium ions. In a solution containing no ammonium salts, characteristic violet precipitates are obtained with magnesium, silver and lead.

Ferrous salts and hyposulfites reduce resorufin and must be removed.

**Detection of hyposulfites, ferrous salts, hypochlorites and dichromates.**

An alkaline solution of resorufin exhibits a yellow-red fluorescence, but upon reduction hydroresorufin is formed which does not fluoresce.<sup>4</sup> Various reducing agents can be detected in this way. Hyposulfite and ferrous iron can be detected as follows:

**Procedure.** Make the solution to be tested alkaline with a little sodium carbonate, and add dropwise a solution containing 0.2 g. of resorufin and 0.2 g. of sodium carbonate in 100 ml. of air-free water. If hyposulfites or ferrous iron are present, no fluorescence appears until an excess of resorufin has been added, but if these ions are absent, an intense fluorescence appears on the addition of the first drop of the reagent. The solution containing hydroresorufin is gradually oxidized on standing in air.

Sulfite, arsenite, thiosulfate, and formaldehyde do not interfere in the test for hyposulfite. Sulfides do not reduce resorufin in cold solution.

Resorufin is oxidized by dichromates in hot dilute sulfuric acid and by hypochlorites in a cold solution. Upon being made alkaline, such solutions show no fluorescence. Potassium permanganate oxidizes resorufin in both acid and alkaline solution.



acid in an acetic acid solution. Warm the mixture to 20-30° C. for several hours. Then heat to 60-80° C., neutralize with sodium carbonate, and salt out.

**Mimosa.** Mimosa is prepared by treating diazotized primuline with ammonium hydroxide.

**Detection of magnesium.** Kolthoff<sup>1</sup> has recommended the use of titan yellow for the detection and determination of magnesium. The test is based on the color change which occurs when a dilute aqueous solution of the dye is adsorbed on precipitated magnesium hydroxide. A 0.01 per cent aqueous solution of titan yellow is pale orange in color, but in the presence of freshly precipitated magnesium hydroxide a rose to red color develops.<sup>6,12,19-21</sup> A pH of 12.5 is necessary to produce the red color. The test proposed by Kolthoff<sup>1,2,7</sup> is carried out as follows:

**Procedure.** Add 0.2 ml. of 0.1 per cent aqueous dye solution to 10 ml. of the solution to be tested, and then add 0.25-0.5 ml. of 4 N sodium hydroxide. In the absence of magnesium this solution is yellowish-brown, but with magnesium the color ranges from orange with 1 mg. per liter to red with 5 mg. per liter. With larger quantities of magnesium, a red flocculation occurs.

By means of a blank for comparison, the sensitivity of the test can be increased to 0.2 mg. of magnesium per liter. Quantities of calcium ranging from 20-200 mg. per liter intensifies the red color. The magnesium test can be carried out on a spot plate by a method recommended by Otto and Otto.<sup>9</sup>

**Procedure.** Place on a spot plate 1 drop each of the magnesium solution, a 0.01 per cent solution of titan yellow, and 2 N sodium hydroxide. In the absence of magnesium the color is yellow, and in the presence of magnesium the color is pink. Magnesium can be detected at a concentration of 0.01 mg. per ml.

The reaction of titan yellow with magnesium is not specific, but is given by many cations. The various color reactions are dependent upon the concentration of the ions and of titan yellow, and upon the pH of the solution. Cadmium, calcium, cobalt, copper, lead, lithium, manganese, and nickel react under the conditions used in making the test. Barium, calcium, and cadmium intensify the red color due to magnesium, and this is probably due to their coprecipitation with magnesium under conditions where they would not precipitate alone.<sup>1,7,9</sup>

Chromium, copper, ferrous, ferric, mercurous, mercuric, silver, and permanganate ions interfere, either because of their color or because of the color of the product formed with sodium hydroxide.

With the spot plate method of Otto and Otto,<sup>9</sup> aluminum, lanthanum, and zinc prevent the formation of the red color of titan yellow with magnesium. With the Kolthoff method, aluminum, ammonium, antimony, arsenic, lanthanum, stannous, stannic, and zinc ions prevent the formation of the magnesium color. The addition of a greater quantity of sodium hydroxide in making these tests causes the formation of a red color, but a high concentration of sodium hydroxide in carrying out the magnesium test is not advisable, since this alone may cause a color with titan yellow that may be confused with the magnesium test.

In general, anions have no effect on the reaction. Tartrate and ferricyanide decrease the sensitivity, and permanganate masks the color.

Barium, bismuth, potassium, sodium, strontium, acetate, arsenate, arsenite, borate, bromide, carbonate, chlorate, chloride, chromate, cyanide, cyanate, ferrocyanide, iodide, nitrate, sulfate, sulfite, thiocyanate, and thiosulfate do not interfere with the magnesium test.

Aluminum salts, which prevent the magnesium reaction, cannot be removed by precipitation with ammonium hydroxide, since most of the magnesium is entrained and lost by this procedure. Zinc can be removed with sodium sulfide. Nickel and cobalt give colorations similar to that with magnesium, but these do not develop in the presence of potassium cyanide. Beryllium does not interfere, but reduces the sensitivity of the magnesium test.<sup>7</sup>

Egriwe,<sup>4</sup> Barnes,<sup>5</sup> and others<sup>28-33</sup> have also used titan yellow as a reagent for magnesium. Smith<sup>8</sup> has also used the dye as a test for magnesium in a group which includes manganese, zinc, cobalt, nickel, calcium, barium, strontium, and magnesium, and in the presence of phosphates. The dye has also been used in a systematic scheme of analysis.<sup>20,21</sup>

Kolthoff prefers titan yellow to quinalizarin for the magnesium test.<sup>3</sup>

Broda<sup>10</sup> has found titan yellow a suitable reagent for observing the distribution of magnesium compounds in plants when these magnesium compounds are known to be present. A microsection is stained with 1-2 drops of a reagent prepared by mixing 1 ml. of a 0.2 per cent aqueous solution of the dye with an equal volume of 10 per cent sodium hydroxide. Magnesium compounds are colored rose with this reagent. This reaction is used only as a confirmatory test since it is not specific.

**Determination of magnesium.** The formation of the red lake of magnesium with titan yellow can be used for the colorimetric determination of small quantities of magnesium.<sup>1,5</sup> When magnesium hydroxide is precipitated in the presence of titan yellow by the addition of sodium hydroxide, the yellow color of the dye changes to a red or orange. With magnesium solutions containing not more than 3 p.p.m. of magnesium the lake remains dispersed for a long time. In the presence of protective colloids such as starch, agar, or dextrin, no precipitate forms even with larger quantities of magnesium. The suspension appears clear and may be compared colorimetrically with standards similarly prepared. Since the color is a mixture of red and yellow, measurement with a colorimeter appears to be desirable.<sup>24</sup> In the presence of calcium, the color of the magnesium lake is deeper, and the suspension shows a minimum transmittance at a wave length of 525  $m\mu$  when compared spectrophotometrically with a suitable blank. Sucrose is used to minimize the effect of calcium. Transmittency readings are reproducible and sufficiently constant to allow time for precise measurement.<sup>23</sup> Color fading is prevented by adding hydroxylamine hydrochloride.

Interference has been discussed in the preceding section on the detection of magnesium.

The following method is described by Gillam:<sup>12</sup>

**Reagent.** Dissolve 0.15 g. of titan yellow in 75 ml. of 95 per cent ethyl alcohol and 25 ml. of distilled water.



**Procedure.** Precipitate iron, aluminum, and phosphorus as iron and aluminum phosphate,<sup>36</sup> and remove calcium by precipitating as the oxalate. Collect the filtrates from the above separations and evaporate to dryness. Destroy ammonium salts by ignition, and dissolve the residue in water. If necessary, add a few drops of acid to facilitate solution.

Dilute the solution to a suitable volume, and transfer an aliquot to a 100-ml. flask. Add exactly 10 ml. of 5 per cent sucrose solution (if calcium is present), and 2 ml. of a 4 per cent solution of hydroxylamine hydrochloride. Add 10 drops of the titan yellow solution, and dilute the mixture to approximately 70 ml. with distilled water. Finally, add 10 ml. of a 4 per cent solution of sodium hydroxide to the solution in the flask while agitating gently. Dilute to volume, mix thoroughly, transfer to the optical cell, and read in a photometer. The magnesium concentration is obtained by reference to a standard curve prepared from solutions containing known quantities of magnesium and treated in exactly the same way as the unknown.

The following method is used for the determination of magnesium in sea water:<sup>22</sup>

**Procedure.** To 5 ml. of distilled water in a test tube, add 1 drop of sea water, 1 drop of a 0.1 per cent solution of titan yellow, and 1 drop of 20 per cent potassium hydroxide solution. Mix and compare the color with a series of standards containing known quantities of magnesium.

This method is also useful for the determination of magnesium in urine. Becka<sup>25</sup> has used a similar method for the determination of magnesium in blood, serum, plasma, urine, meats and other organic materials.

Muller-Neugluck<sup>13,14</sup> has applied this method to the determination of magnesium in boiler feed-water. Nitrate, nitrite, bicarbonate, carbon dioxide and ammonium salts do not affect the color, but all traces of iron, manganese, aluminum, silicon, and organic compounds must be removed by treatment with ammonium chloride, ammonium hydroxide and animal charcoal.

Urbach and Baril<sup>15</sup> have determined magnesium with titan yellow, using a step photometric method which does not require standard solutions.

Kreibich and Bäumlér,<sup>11</sup> Sinigaglia<sup>26</sup> and Sloss<sup>24</sup> have used titan yellow to determine magnesium in aluminum and aluminum alloys, and Gillam<sup>12</sup> has used a similar method for determining magnesium in soils and fertilizer. The method may also be applied to the determination of magnesium in lead.<sup>27</sup>

In the color reaction for magnesium, a state of equilibrium exists between the dyestuff and the color lake. Ginsberg<sup>16</sup> has determined the value of this equilibrium at various concentrations, and from these data has constructed a curve for the interpretation of his results. The points on the curve do not correspond to the formation of a definite lake, and the intensity of the color does not increase indefinitely but reaches a maximum. The lake formation, therefore, follows the simple laws of adsorption. A mathematical analysis shows that a color comparison in the presence of both lake and dyestuff is justified, but the dye must always be present in excess.

**Detection of boron.** Boric acid can be detected by the red color which it yields with tincture of mimosa flowers.<sup>17,18</sup>

**Reagent.** Place 5 g. of carefully selected mimosa blossoms in a small beaker, add 50 ml. of 95 per cent alcohol, and heat 10 minutes on a water-bath. Cool thoroughly and filter. Extract a second time, using 40 ml. of alcohol. Filter, and express the residue with a spatula. Store in a glass-stoppered bottle in a dark place.

**Procedure.** Mix 2 drops of alcoholic extract of mimosa with 5 drops of water, 3 drops of 20 per cent sodium carbonate, and 2 drops of a hydrochloric acid solution to be tested. Evaporate the mixture in a porcelain dish to dryness on a steam-bath. Moisten the cooled residue with ammonia. As little as 0.0004 mg. of boric acid per ml. gives a rose color.

Tartaric acid, citric acid, oxalic acid, and acetic acid must be removed by ignition before making test.

This method for detecting boric acid is excellent for detecting boron in milk, wine, and other food products. Robin<sup>17</sup> considers this method more sensitive than that with curcuma.

1. I. M. Kolthoff, *Chem. Weekblad*, **24**, 254-5 (1927); *C.A.* **21**, 2632 (1927).
2. I. M. Kolthoff, *Biochem. Z.* **185**, 344-8 (1927); *C.A.* **21**, 3580 (1927).
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4. E. Eegriwe, *Z. anal. Chem.* **76**, 354-9 (1929); *C.A.* **23**, 2903 (1929).
5. H. D. Barnes, *J. S. African Inst.* **11**, 67-8 (1928); *C.A.* **23**, 1838 (1929).
6. J. V. Dubsky and A. Okac, *Chem. Listy*, **24**, 492-3 (1930); *C.A.* **25**, 2660-1 (1931).
7. I. M. Kolthoff, *Mikrochemie, Emich Festschr.* 180-90 (1930); *C.A.* **25**, 3267 (1931).
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### TOLUYL ORANGE R(S)

Synonym: Direct orange R, toluylene orange R

$C_{28}H_{28}N_8O_6S_2Na_2$

Mol. Wt. 682.62

Color Index, 446.

**Use:** Detection of magnesium.

Toluy Orange R(S) is a brownish-red powder. It dissolves in water to form an orange-yellow solution, and in sulfuric acid to form a brown solution.

**Preparation:** Tetrazotize 31 g. of tolidine sulfate with 25 g. hydrochloric acid ( $d = 1.16$ ) and a solution of 14 g. sodium nitrite, and add to a faintly alkaline solution containing 44 g. of the sodium salt of *m*-toluylenediamine sulfonic acid in 1 liter of water. Stir and salt out.

**Detection of magnesium.** Eegriwe<sup>1</sup> reports the use of toluy orange as a reagent for magnesium, although according to Dubsky and Okac<sup>2</sup> only a vague color change is obtained with this dye in the presence of magnesium hydroxide. This test is based on the adsorption of the dye by precipitated magnesium hydroxide.

**Procedure.** Add 1-2 drops of a 0.01 per cent aqueous solution of the dye to one drop of the solution to be tested, and then make alkaline with an excess of 2 N sodium hydroxide. An aqueous solution of the dye is yellow, but in the presence of as little as 0.01 mg. of magnesium the color is orange-yellow.

The test may be made in the absence of nickel, cobalt, and chromium. Karaoglanov<sup>3</sup> and Heller<sup>4</sup> have included this reagent in a study of magnesium reagents.

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### TURMERIC

Synonym: Curcumin

$C_{21}H_{20}O_6$

Mol. Wt. 368.37

Color Index, 1238.

$HO(CH_3O)C_6H_3-CH=CH-CO-CH_2-CO-CH=CH-C_6H_3(CH_3O)OH$

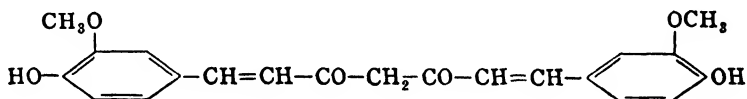
**Use:** Detection of barium, beryllium, boron, calcium, hafnium, magnesium, molybdenum, titanium, tungsten, uranium and zirconium.

Determination of beryllium, boron and magnesium.

Turmeric is obtained from curcuma, the rhizome of *Curcuma Longa L Zingiberaceae*, which consists of about 5 per cent volatile oil with the yellow coloring

matter, curcumin, starch and resin. The compound is an orange-yellow crystalline powder which melts at 183° C. It is insoluble in water and ether, but dissolves in alcohol and glacial acetic acid. It reacts with alkalis to yield a brown-red color and with acids to give a light yellow color.

**Detection of boron.** When a solution of turmeric is evaporated with boric acid, a deep red colored product is formed. This reaction depends upon the conversion of the diferuloylmethane (yellow curcumin)



into the isomeric reddish-brown rosocyanine by the action of boric acid. An intermediate compound consisting of an unstable addition product of boric acid and turmeric is formed.<sup>1-3</sup> The rosocyanine formed in this reaction is converted to a blue to greenish-black compound in the presence of alkalis, although the original red-brown color is restored when treated with acids. Ferric, molybdenum, titanium, columbium, tantalum, and zirconium compounds also change turmeric to a red-brown compound; but this, unlike that formed with boric acid, does not change to blue or green upon treating with an alkali. The color reaction of boric acid with turmeric has been extensively used as a test for boron.<sup>4-10</sup> The test for boric acid can be carried out on a glass plate, on filter paper impregnated with turmeric, or in a small test tube.

**Procedure.** Mix 1 ml. of the solution to be tested with 1 ml. of concentrated hydrochloric acid and place a drop of this mixture on a glass plate. Mix with 0.1 ml. of an aqueous solution of turmeric and observe the color. As little as 1γ of B<sub>2</sub>O<sub>3</sub> can be detected by means of the red color which is formed.

Boron can be detected by means of a spot test carried out as follows:

**Procedure.** Soak a strip of quantitative filter paper in tincture of curcuma and allow to dry. Acidify the solution to be tested with hydrochloric acid and place a drop of the resulting mixture on a small strip (3 x 7 mm.) and dry at 100° C. A red-brown spot appears with boric acid, and this turns blue to greenish-black on treating with 1 per cent solution of sodium hydroxide. By means of this test as little as 0.01γ of boron can be detected at a concentration of 1:2,500,000.

The turmeric reaction is prevented by oxidizing substances, such as hydrogen peroxide, chlorates and by iodides; and consequently these must be decomposed before carrying out the test.

The test may be carried out in the presence of chromate, permanganate, hypochlorite, and other strong oxidizing agents by allowing the boric acid to rise by capillarity in filter paper. The oxidizing agents are reduced in the lower part of the paper.<sup>44</sup> In the presence of chlorate it is important to prevent the

solution from becoming too acid during the drying. This is accomplished by acidifying the solution to be tested with a saturated solution of potassium acid sulfate rather than with hydrochloric acid.<sup>44</sup>

Fluoride tends to prevent the turmeric reaction, but larger quantities of boron can be detected in the presence of considerable fluoride. Tin, zirconium, molybdenum and tungsten may interfere with the boron test since they too give color reactions with turmeric. There is, however, little danger of mistaking the color caused by these ions for that resulting from the action of boric acid.

According to Low<sup>4</sup> it is not necessary to dry the paper at a temperature of 100° C. Paper dried in air or in a vacuum desiccator at room temperature or at 40-50° C. gives good results. This procedure allows the detection of boric acid in the presence of large quantities of other salts such as nitrates and phosphates where it would be overlooked entirely when ordinary methods are employed. Marken<sup>45</sup> has pointed out that certain turmeric papers contain boron and consequently give a positive test even in the absence of boron in the test solution.

Lenher and Wells<sup>7</sup> have found the turmeric test to be delicate but in some instances unreliable. If a little too much acid is used to convert borates to boric acid, the reagent paper will, when dried, be brown instead of pink. On the other hand, in the presence of an insufficient quantity of acid, there will be no coloration due to boric acid.

Brinsmaid<sup>5</sup> has recommended a procedure for the detection of boric acid based upon a special method of preparation of the turmeric test paper. This is carried out as follows:

**Reagent.** Treat 30 g. of freshly ground turmeric with a mixture of 180 ml. of 95 per cent alcohol and 120 ml. of water. Evaporate to dryness on a steam-bath, cool and add 10 ml. of alcohol. If all of the red, oily material does not dissolve, add alcohol in small portions with decantation until the red product has passed into solution. The brown scaly material does not dissolve. Filter the mixture through paper, wash until clear with alcohol, and dilute with alcohol to 100 ml. Prepare a paper pulp by disintegrating filter paper which has been washed with hydrochloric and hydrofluoric acids. For each gram of the dry pulp, place in a beaker 75 ml. of water and 15 drops of the turmeric solution. Add the paper pulp and stir thoroughly. Place the mixture on a steam-bath and allow to stand until the paper has adsorbed all of the coloring matter. Filter through a Buchner funnel fitted with a sheet of filter paper. Add the pulp suspension in such quantity that when it has been sucked dry, a layer of approximately 3 mm. in thickness will remain. Do not wash. When the mixture is dry, remove the bottom sheet of filter paper and cut the mass into squares of about 7 × 8 mm. Place in a tight container and store in a dark place.

**Procedure.** To test for boric acid, place one of the little squares of paper which has been impregnated with turmeric in a depression of a spot plate and moisten with a few drops of the acid solution to be tested. The paper should be thoroughly moistened with the solution. Place the plate in a warm place and allow to dry. The paper should be thoroughly dry but should not be overheated.

A pink to red color appears in the presence of boric acid and this changes to a clear blue on the addition of 1-2 drops of 0.1 N sodium hydroxide solution.

Chamot and Cole<sup>8</sup> have modified the turmeric test by using threads of viscose silk which have been impregnated with turmeric.

**Reagent.** Boil 200 g. of curcuma with 50 ml. of alcohol, filter, and mix the filtrate with 50 ml. of water. Add 1 ml. of 10 per cent sodium hydroxide solution to the curcuma extract and soak threads of viscose silk in this solution. Evaporate the wet threads until the mass becomes syrupy, and then immerse in 0.5 per cent alcohol and press between filter paper. Then place in dilute sulfuric acid and finally wash with water and dry.

**Procedure.** Place a drop of the solution to be tested on a microscope slide and acidify with drop of hydrochloric acid. Place one of the impregnated silk threads in this mixture and evaporate by warming gently. If boric acid is present the thread is colored red-violet, and this changes to a blue color on treating with 1 per cent sodium hydroxide solution.

Molybdenum, titanium, zirconium and tantalum salts do not interfere with the test when carried out in this manner. Phosphoric and silicic acids decrease the sensitivity somewhat.

Michel<sup>9</sup> has recently proposed a test for boric acid which he claims to be more sensitive and more specific than those previously used. His procedure is as follows:

**Procedure.** Add 1 or 2 drops of a 0.1 per cent alcoholic solution of curcumin to a solution containing free boric acid or a borate that has been acidified with hydrochloric acid, and then add a few drops of pure ethyl alcohol, a little salicylic acid, and a drop of 6 N hydrochloric acid. Stir in a small porcelain dish and evaporate on a water bath. If only a trace of boric acid is present, the residue is strongly colored red. Dissolve the residue in a little ethyl alcohol and again evaporate. The spot ordinarily shows a greenish fluorescence with this treatment. Again dissolve in a few drops of ethyl alcohol and add a few drops of 6 N ammonium hydroxide solution. A corn-flower blue color appears.

Wade and Wade<sup>10</sup> have found that boric acid can be detected by exposing turmeric paper to the vapors of methyl borate. Since boric acid is commonly separated from interfering substances by converting to the volatile methyl ester, this procedure offers the advantage that it is unnecessary to convert the methyl borate to boric acid by means of an additional step in the procedure.

**Procedure.** Mix 0.1 g. of a mineral borate with 0.5 ml. of hydrochloric acid and 10 ml. of methyl alcohol. Evaporate this mixture to a small volume while holding a moistened strip of turmeric paper in the vapors which are formed. A characteristic red color occurs with boric acid. The strip of turmeric paper is then attached to the inside of a beaker in a vertical position so as to dip into a little distilled water containing a few drops of ammonia. A pink to

deep purple or blue color is formed, which is in marked contrast with the red part of the paper which is unaffected by the vapor.

A spectrophotometric method for detecting boron has been proposed by Holmes.<sup>13,14</sup> The principal absorption of turmeric is in the violet end of the spectrum in which accurate measurements of light absorption are difficult. The band extends into the blue region (495-510  $m\mu$ ) which permits a more accurate measurement. The compound formed with turmeric and boron is redder in color than that of turmeric itself and its absorption band lies nearer to the red end of the spectrum than that of the pure reagent, and absorption in the blue region is proportionately greater. The conversion of turmeric to the boron compound, accordingly, results in increased absorption in that region. Conversely, the demonstration of increased absorption within this region under suitable conditions may be used for the detection of boron. The procedure is as follows:

**Procedure.** Extract turmeric with 95 per cent alcohol, and dilute with 95 per cent alcohol to such an extent that 100 ml. of the resulting solution contains 50-60 mg. of total solids. Place 1 ml. of the aqueous solution to be tested in a porcelain dish and acidify with 1 ml. of glacial acetic acid, and then add 2 ml. of the turmeric solution. Evaporate to dryness on a steam-bath and dissolve the residue in 5 ml. of glacial acetic acid. Prepare a blank simultaneously and in the same manner by using 1 ml. of distilled water instead of the solution to be tested. Determine the extinction coefficient of the final acetic acid solutions in 2-cm. layers over the spectral range between 495-510  $m\mu$ . If boron is present the extinction coefficient of the test solution will be greater than that obtained with the blank. With duplicate or triplicate determinations, it is possible to detect 1 part of boron in 25,000,000 parts of an aqueous solution.

**Determination of boron.** The color formed in the reaction between turmeric and boric acid can be used for the colorimetric determination of small quantities of boron. Bertrand and Agulhon<sup>20-28</sup> have proposed a method in which a strip of turmeric paper is immersed in a solution containing boric acid and the boron content is estimated from the height of the red coloration. The following method may be applied to the analysis of plant or animal material:

**Reagents.** *Turmeric paper:* Cut a good grade of drafting paper into strips about  $3 \times 45$  mm. in size, and soak in an alcoholic solution of turmeric. Make the saturation as uniform as possible. Squeeze out the excess reagent, and dry the strips.

*Standard borate solution:* Dissolve 0.2739 g. of sodium tetraborate,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ , in water, mix thoroughly, and then dilute to one liter. Again mix. One ml. of this solution contains 0.1 mg. of  $\text{B}_2\text{O}_3$ .

**Procedure.** Ash 10-20 g. of material if of animal origin or 0.5-1.0 g. if of plant origin in a platinum dish at the dull red heat in the presence of sodium carbonate. Add 5-10 ml. of phosphoric acid and pour the mixture into a 200-ml. flask. Rinse the dish with 20 ml. of methyl alcohol and add the rinsings to the material in the flask. Distill on a steam-bath and collect the distillate in a

platinum capsule containing a few drops of N sodium carbonate solution. Add 10 ml. of methyl alcohol to the distillate and distill a second time. Evaporate the distillate to dryness and cool, and add 4 drops of 10 N hydrochloric acid and 0.5 ml. of water. With the aid of distilled water transfer the wash solution into a small glass vial, 30 mm. in height, and with a volume of 1.5 ml. shown by a mark. Immerse a strip of the turmeric paper ( $3 \times 45$  mm.) in this solution to a depth of 15 mm. Heat the mixture for 3 hours at  $35^{\circ}\text{C}$ . and determine the height of the red coloration in mm. The amount of boron in the unknown can be estimated by comparing the height of the color with that obtained with a set of standards prepared by immersing similar strips of turmeric paper in solutions containing known quantities of boron. Similar results may be obtained by allowing the strips of paper to remain in contact with the solution for 10-24 hours at ordinary temperatures instead of heating for 3 hours at  $35^{\circ}\text{C}$ . By this method it is possible to determine 0.0005-0.1 mg. of boron.

Small quantities of boron may also be determined by the use of a solution of turmeric, rather than with the aid of turmeric paper.<sup>27-29,45</sup> The following procedure may be used:

**Procedure.** Proceed exactly as in the above method, except that the residue obtained from the evaporation of the distillate is dissolved in one ml. of water and 2 ml. of hydrochloric acid (d. 1.162). One ml. of a solution of turmeric in ethyl acetate is then added to the sample and to each of the standards, which have been similarly treated and which contain known amounts of boron. Color comparison is made after 50 minutes.

A red color is obtained when a solution of turmeric is added to concentrated hydrochloric acid, but if water is added to this solution, the red color gradually changes to yellow. A solution prepared by mixing 1 ml. of turmeric solution with 20 ml. of concentrated hydrochloric acid shows distinct differences in color upon dilution with 5, 10, 15, 20 and 25 ml. of water. If boric acid is added to the diluted solution, a color change from yellow to red takes place. This color change is more sensitive in concentrated hydrochloric acid solutions, but for a colorimetric estimation of boron, dilute hydrochloric acid solutions are more suitable. Since the changes in color vary with the boron content of the solution, a comparison of colors may be used for a satisfactory colorimetric determination of boron.<sup>30</sup>

Cassal and Gerrans<sup>31-33</sup> have found that the addition of oxalic acid increases the sensitivity of the turmeric-boric acid reaction. These investigators have used a colorimetric method for determining boron in which the color is allowed to develop in tincture of turmeric and the resulting mixture evaporated on a sand-bath with the aid of heat, but this causes a loss of boric acid through volatilization. In order to prevent this the boric acid is trapped in potash bulbs and redetermined. This necessarily causes considerable loss of time and accuracy in making the final determination. According to Robinson<sup>34</sup> the volatility of boric acid is due largely to the presence of ethyl alcohol which is used as a solvent for the turmeric. In order to overcome this, Robinson has proposed the use of a turmeric reagent which requires no alcohol in its preparation.



Phosphate, silicate and salts of sodium and potassium hinder the development of the red color with turmeric, and must be absent when making the determination. The most convenient method of separating boron from interfering substances is to treat the plant ash with phosphoric acid and methyl alcohol and to distill the boron as methylborate, and then to collect the distillate in solutions of alkalis. The use of sodium hydroxide as a receiving alkali in this distillation causes diminution in the amount of color developed by a given quantity of boron. When a constant quantity of boron is used, and increasing quantities of sodium hydroxide are added to it, an increasing depression of the color with turmeric occurs until a maximum depression is reached. A further increase in the quantity of sodium hydroxide used causes no further depression. Consequently, by employing a suitable and constant excess of sodium hydroxide as a receiving solution for the methyl borate, no difficulty is encountered within a given range of boron contents. The effect of sodium hydroxide upon varying amounts of boric acid is shown in Table 55.

TABLE 55.—EFFECT OF SODIUM HYDROXIDE UPON THE COLOR OF BORIC ACID

Mg. $B_2O_3$ Present	Lovibond Red Units	
	No NaOH Added	4 ml. N/50 NaOH
0.005	2.0	1.0
0.010	4.0	2.0
0.015	6.0	3.0
0.020	8.0	4.8
0.025	10.0	5.7
0.030	12.0	7.3

The procedure recommended by Robinson is as follows:

**Reagent.** Extract 20 g. of powdered turmeric in a Soxhlet apparatus until the syphonings are colorless, and then dilute the yellow extract to 250 ml. with ether.

The sensitivity of turmeric is diminished somewhat by contact with air, and so different samples of the reagent may vary in their effectiveness in the boric acid reaction. As a result, the quantities of turmeric recommended in the following steps may have to be increased in some instances to insure that an excess of the reagent is used.

Mix 4 ml. of the ether extract prepared above with 40 g. of acid-washed silver sand. Mix thoroughly and evaporate on a water-bath so that the particles of sand are covered with turmeric. Use 40 g. of this material as the reagent. To standardize, evaporate to dryness convenient quantities of standard boric acid, each with 0.5 ml. of N sodium hydroxide solution. Add 1 ml. of water and 1 ml. of saturated oxalic acid solution to each and dissolve the residue. Add 40 g. of

the turmeric-covered sand and stir well, and evaporate to dryness on a water-bath. Add 1 ml. of a saturated solution of oxalic acid, mix, and again evaporate to dryness.

Transfer the mixture to a Jena sintered glass filter funnel (No. 11G1) and extract with 70 per cent alcohol until the filtrate is colorless. Dilute the extract to 100 ml., and estimate the color by means of a Lovibond tintometer. Since varying quantities of unchanged yellow turmeric are present in the solution, it is impossible to estimate accurately the red color produced in the boric acid reaction with an ordinary colorimeter. It is necessary to employ an instrument which can eliminate differences in tints. The color is stable for 3 hours even in sunlight, but after this time it begins to fade slowly.

**Procedure.** Ash about 1 g. of plant material with a solution of barium hydroxide and remove the boron by distillation with methyl alcohol and phosphoric acid. Collect the distillate in a receiver containing 0.5 ml. of N sodium hydroxide, and evaporate to dryness. Treat the residue exactly as described in the method for preparing the standard.

Hawley<sup>17,18</sup> has used turmeric for an approximate colorimetric determination of boron in butter.

**Detection of beryllium and magnesium.** In weakly alkaline solutions, turmeric is adsorbed by beryllium hydroxide with the formation of an orange-red color, which can be used for the detection of beryllium. The following procedure is recommended by Kolthoff:<sup>35</sup>

**Procedure.** To 10 ml. of the solution to be tested, add not more than 1 drop of 0.1 per cent alcoholic turmeric solution, 0.5 ml. of 4 N ammonium chloride and 6-8 drops of 4 N ammonia. A red precipitate forms if beryllium is present. A blank similarly prepared is yellowish-brown in color. By this method 0.05 mg. of beryllium can be detected in 1 liter of solution.

Sodium, potassium, lithium, calcium, and barium do not interfere with this test, but magnesium causes a decrease in the sensitivity of the reaction.

In strongly alkaline solutions, beryllium does not give a color reaction with turmeric, since beryllium hydroxide redissolves. Under these conditions, magnesium gives a test with turmeric, although this is not as sensitive as the reaction with titan yellow.

**Procedure.** Add 1 drop of the turmeric solution to 10 ml. of the solution to be tested, and make alkaline with 1 ml. of 4 N sodium hydroxide. An orange to orange-brown color appears, depending upon the concentration of magnesium. As little as 1 mg. of magnesium per liter can be detected by this method.

Ferric iron and aluminum also form colored lakes with turmeric, but this interference can be eliminated by the addition of an excess of sodium fluoride. Ferric ions also may be precipitated at room temperature with an excess of sodium hydroxide. This latter procedure is preferable, since sodium fluoride decreases the sensitiveness of the beryllium reaction.

Magnesium may be detected by means of the reddish-brown fluorescence which is observed when a magnesium salt solution is treated with turmeric and viewed under ultra-violet light.<sup>38</sup>

**Determination of beryllium and magnesium.** Kolthoff<sup>35</sup> and Thompson<sup>43</sup> have used the formation of the beryllium and magnesium lakes with turmeric as the basis for colorimetric methods for determining small quantities of these ions. This method is based upon the formation of a suspension of the magnesium lake, but the color is affected by the presence of phosphate. If, however, the standards used for the comparison contain an equivalent quantity of tricalcium phosphate, the color intensities are comparable and in proportion to the amount of magnesium present.

Thrun<sup>36,37</sup> has used starch glycerite to render the method of Kolthoff more sensitive and to retard the settling of the magnesium lake. The following method for determining small quantities of magnesium in biological fluids or ash, and in the presence of phosphate, has been proposed by Thrun.<sup>36,37</sup>

**Reagent.** *Starch glycerite:* Triturate 10 g. of starch with 20 ml. of water until the mixture is homogeneous, and then gradually add this mixture to 70 ml. of glycerol contained in a porcelain dish. Heat to about 140° C. and continue the heating (while keeping the temperature below 144° C.) with constant stirring until a translucent jelly is formed.

**Procedure.** Place the solution of the ash (or a suitable aliquot) containing about 2 ml. of concentrated hydrochloric or nitric acid per liter, and equivalent to about 0.02-0.04 mg. magnesium in a 50-ml. Nessler tube or volumetric flask and dilute to 40 ml. Now add 2 ml. of a starch glycerite solution prepared by shaking a little of the jelly with water and filtering, and then add 4 drops of a 1 per cent alcoholic solution of turmeric. The turmeric solution should be measured exactly from the capillary pipet, and the same quantities should be added to both unknown and standards. Mix thoroughly, and add 5 ml. of 4 N sodium hydroxide. Mix, dilute to the mark, and again mix. Compare the resulting color with that of standard solutions similarly prepared.

A standard solution containing 0.02 mg. of magnesium per ml. is prepared by dissolving 0.203 g. of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  and 0.1-0.4 g. of tricalcium phosphate in water containing 2 ml. of concentrated nitric acid and diluting to 1 liter.

It is possible by this method to distinguish differences of 0.01 mg. of magnesium. The color intensity of the reaction is such that the depth of the liquid should be greater than 5 ml. The suspension is stable for several hours.

Iron may precipitate upon the addition of sodium hydroxide and dilution with water and in this case it should be removed as follows: Titrate a separate aliquot with dilute sodium hydroxide to the neutral point with methyl red, and then add the same amount of sodium hydroxide to the aliquot to be used in the determination. Remove the precipitated ferric hydroxide by filtration or with the aid of a centrifuge. At the pH (4-5) at which the ferric hydroxide is precipitated, magnesium phosphate remains in solution.

If more than 0.6 mg. of  $B_2O_3$  is present in the solution, magnesium-free blanks are affected slightly. This interference is eliminated by the removal of boron as volatile methyl borate.

Goto<sup>38</sup> has recommended determining magnesium colorimetrically by means of the intensity of the reddish-brown fluorescence which is obtained when a mixture of a magnesium salt and turmeric is viewed under ultra-violet light.

#### Detection of zirconium, hafnium, titanium, molybdenum and tungsten.

Zirconium may be detected by means of a color reaction with turmeric and a hydrochloric acid solution of the metal salt. If a dilute solution containing the zirconium salt is mixed with an equal volume of concentrated hydrochloric acid and a little turmeric solution is added, the pale yellow color of the reagent is changed to a deep orange. As little as 0.2γ of zirconium can be detected by means of this reaction. The presence of sulfates makes the test less sensitive, and phosphate and fluoride prevent it entirely. Bismuth, titanium, tungsten and molybdenum, also give color reactions with turmeric and consequently interfere with the zirconium test.<sup>39,42</sup>

Hafnium reacts like zirconium.<sup>42</sup>

Titanium may also be detected if a solution of titanium tetrachloride is diluted with an equal quantity of concentrated hydrochloric acid and treated with a little turmeric solution. In this way 0.5γ of titanium can be detected. The interference for this reaction is the same as that described above for zirconium.

Tungsten can be detected similarly, but this reaction is not so sensitive, although 5γ of tungsten can be detected in 1 drop of solution.

**Detection of barium and calcium.** When a solution of a barium salt is treated with fluosilicic acid in the presence of turmeric, the precipitate of the barium salt adsorbs turmeric and yields a brownish-red fluorescence. Goto<sup>40</sup> has used this reaction for the detection of barium, but the test is not sensitive.

Calcium can be detected by the orange-red fluorescence which it yields with turmeric.

**Detection of uranium.** Zimmermann<sup>41</sup> has used turmeric for the detection of uranium. A strip of turmeric paper is colored brown when immersed in a weakly acid solution of uranium nitrate. One ml. of solution containing 1-10 mg. of uranium salts gives this reaction.

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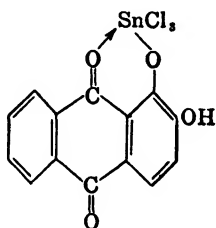
## CHAPTER XV

### HYDROXYANTHRAQUINONE DYES

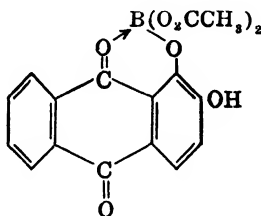
The use of the hydroxyanthraquinone dyes as analytical reagents has steadily increased since Attack first discovered in 1915 that alizarin red S (sodium salt of alizarinsulfonic acid) could be used to detect aluminum. Excellent methods have since been proposed for the detection and colorimetric determination of magnesium, beryllium, aluminum, boron, fluoride, zirconium, indium, gallium, lanthanum, hafnium, and other metals, using these dyes.

The value of the hydroxyanthraquinone derivatives as analytical reagents, however, has been limited somewhat by the fact that similar lakes are formed with nearly all cations, and that these lakes are so strongly colored that it is difficult to differentiate between small quantities of the lake and large quantities of the dye. Further, these dyes give reactions which are generally less sensitive than those with dithizone, which also reacts with many ions. On the other hand the hydroxyanthraquinone dyes are easily prepared and possess excellent keeping qualities, and this to some extent counteracts the more serious objections to their use.

Alizarin, and other hydroxyanthraquinone dyes having a hydroxyl group in the 1-position, have an atomic grouping similar to that found in the enol forms of the 1,3-diketones, and consequently are capable of forming inner-complexes with the metals, and also with acids. Typical of the former is the compound with stannic chloride, prepared by Pfeiffer.<sup>1</sup>



An example of the complexes with acids is the boroacetic ester,

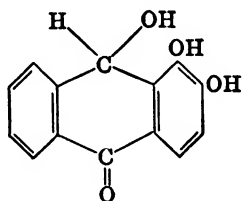


isolated by Dimroth and Faust.<sup>2</sup> The coordination of the carbonyl oxygen atom to the boron atom may account for the intense color change which occurs when

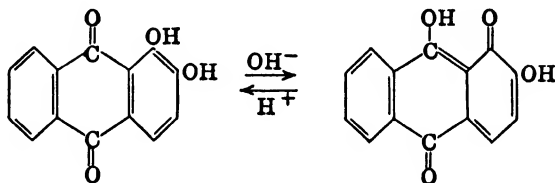
borates are added to sulfuric acid solutions of various hydroxyanthraquinone dyes. Many of these reactions have been used for the detection of boron.<sup>3,4</sup>

The inner-complexes of alizarin with metals, particularly aluminum and zirconium, are of especial interest, since their formation constitutes very sensitive tests for these metals. If aluminum hydroxide is treated with an ammoniacal solution of alizarin, a red-violet color appears, which cannot be removed by washing. A red-brown precipitate of  $\text{Al}(\text{C}_{14}\text{H}_7\text{O}_4)_3$  is formed when the monopotassium salt of alizarin is added to aluminum chloride.<sup>5,6</sup> Analogous chromium and iron salts have been prepared in a similar manner. It appears likely that such compounds are contained in the color lakes formed in dyeing with turkey red, but these lakes contain in addition bivalent metals, usually calcium, and also hydroxy fatty acids.<sup>7</sup>

The coordination of the metal atom with the oxygen of the carbonyl group adjacent to the hydroxyl group is indicated by the fact that deshydroxy alizarin



under similar conditions forms no colored aluminum compound. Further, 1-hydroxyanthraquinone reacts with an ammoniacal solution of a cupric salt to decolorize the blue solution and form a red-violet precipitate, while 2-hydroxyanthraquinone has no similar effect. It should be noted, however, that the formation of intensely colored aluminum compounds does not necessarily indicate inner-complex formation, since nearly all polyhydroxyanthraquinones undergo a deepening of color when their salts are formed, regardless of the position of the hydroxyl groups. In most cases, also, when the alkali soluble hydroxyanthraquinones are dissolved in basic solutions, a deepening in color occurs, which can be reversed by acids. Exceptions to this behavior are the 1,7- and 1,8-dihydroxyanthraquinones, which show no color change when dissolved in alkalies.<sup>8</sup> It is not known definitely whether the deepening in color is caused simply by the formation of the salt of the hydroxyanthraquinone, or whether, in addition, there is a rearrangement in the molecule.



According to Meyer and Fischer,<sup>9</sup> however, salt formation plays a definite role in the color change.

It seems certain that adsorption phenomena play an important part in the formation of color lakes. For example, 1,2-, 1,3-, 1,4-, 1,5-, 1,7-, and 2,3-

dihydroxyanthraquinones are taken up from pyridine-ammonia solutions by freshly precipitated aluminum hydroxide that has been washed with acetone to form colored products that are resistant to acetone. On digesting with hot ammonia, these products become colorless. This may indicate the occurrence of adsorption preceding the formation of a salt. That salt formation does occur, however, is indicated by the fact that a color change or precipitation occurs when an ammoniacal solution of 1,2-, 2,3-, or 1,4-dihydroxyanthraquinone, or 1,2,3-trihydroxyanthraquinone is added to a solution of an aluminum salt containing a tartrate. In the presence of a tartrate, aluminum hydroxide is not precipitated by the addition of the ammoniacal solution, and hence adsorption of the dye is impossible.

Zirconium salts react with the hydroxyanthraquinones, even in solutions of mineral acids, to form red to blue precipitates, or cause color changes in the dye solution. These reactions can be used for the detection of zirconium, and also fluoride, since the latter forms a stable complex anion with zirconium. Alcoholic solutions of 1,2-, 1,4-, 2,3-, 2,6-, and 2,7-dihydroxyanthraquinone, 1,2,4-trihydroxyanthraquinone, and 1,4,5,8-tetrahydroxyanthraquinone give colored precipitates with solutions of zirconium salts in the presence of mineral acids. It will be noted that an hydroxy group in the 1-position is apparently not necessary for the zirconium reaction.<sup>10</sup> 1- and 2-monohydroxy-, and 1,3- and 1,5-dihydroxyanthraquinone give no similar reaction, but they are capable of coloring freshly precipitated zirconium hydroxide.

The hydroxyanthraquinones appear capable of important selective action in some of their analytical properties. The reactions with the trivalent metals and the rare earths are especially interesting. To illustrate this selectivity, a saturated solution of 1-hydroxyanthraquinone reacts with beryllium but not with aluminum; and 1,3-dihydroxyanthraquinone reacts, in a not too concentrated solution, with calcium but not with strontium or barium.

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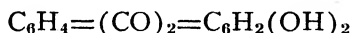
## ALIZARIN

Synonym : 1,2-Dihydroxyanthraquinone

$C_{14}H_8O_4$

Mol. Wt. 240.20

Beil. Ref. VIII, 439.



**Use:** Detection of aluminum, ammonia, copper, columbium, fluoride, gallium, indium, mercury, thorium, titanium, uranium, zirconium.

Determination of aluminum, calcium, fluoride, sodium and zirconium.



Alizarin occurs as an ochre-yellow powder, or as orange-red needles when crystallized from alcohol or obtained by sublimation. It melts at  $290^{\circ}$  (corr.) and sublimes above  $110^{\circ}$ . The commercial compound always contains anthraquinone, 1-hydroxyanthraquinone, and isopurpurin. A method for purifying the commercial product has been described by Boeseken.<sup>2</sup>

Alizarin is soluble in 300 parts of water. It is moderately soluble in alcohol, but is quite soluble in hot methyl alcohol, benzene, ether, glacial acetic acid, carbon disulfide, and pyridine. It is also soluble in alkalies, and the resulting solutions appear blue by reflected light, but purple-red by transmitted light.

**Preparation:** *Sodium anthraquinone- $\beta$ -sulfonate:* Add 30 g. of anthraquinone to 30 g. of 40 per cent fuming sulfuric acid, which is contained in a 250-ml. flask. Fit the flask with an air condenser and heat in a paraffin bath to  $150$ - $160^{\circ}$  C. for 8 hours. While still hot, pour the dark-colored mixture into a dish containing 1 liter of cold water, and boil for 1 hour. Filter off any unreacted anthraquinone with suction, and boil the residue with 500 ml. of water. Filter, and wash once or twice with boiling water. Add 0.2 g. of potassium chlorate to the combined filtrates and washings, and evaporate to a volume of about 500 ml. Pour off 10 ml. of the solution into a test tube, carefully neutralize the remainder with a sodium carbonate solution (about 120 g. crystalline sodium carbonate), and then replace the 10 ml. of solution. In this way the mixture is nearly neutralized, but remains slightly acid. Evaporate on a water bath until a scum covers the surface of the liquid, and then allow to cool. Separate the pale yellow crystals of the sodium salt of the sulfonic acid by filtering with suction. Wash 3-4 times with slightly acidified water, and dry on a porous plate.<sup>5,6</sup>

*Alizarin:* Dissolve 5 g. of potassium chlorate in 50 ml. of water, and to this add 20 g. of sodium anthraquinone- $\beta$ -sulfonate and mix to a paste. To this mixture add a hot solution prepared by dissolving 90 g. of sodium hydroxide in 45 ml. of water. Immediately transfer the resulting paste to a steel pressure tube of such size that it is about two-thirds filled by the mixture. Heat in an oil or paraffin bath for three hours to  $190$ - $200^{\circ}$ . Remove the contents of the tube and digest with boiling water for one hour, and add calcium hydroxide until the calcium alizarinate is completely precipitated. Filter with suction and wash with boiling water until the filtrate is no longer red. Suspend the residue in a large quantity of hot water, and decompose by adding hydrochloric acid. Filter from a cold solution the alizarin, which separates as an orange, flocculent precipitate, wash eight times with cold water, and finally dry and crystallize from alcohol or cumene.<sup>3,4</sup>

Commercial alizarin contains anthraquinone, 1-hydroxyanthraquinone, and isopurpurin. To purify, first treat with a dilute soda solution in which anthraquinone is insoluble. Remove the anthraquinone by filtration, and then precipitate alizarin and 1-hydroxyanthraquinone from the filtrate by treating with carbon dioxide. Isopurpurin remains in solution. Boil the precipitate of the sodium salts of alizarin and 1-hydroxyanthraquinone with barium hydroxide to dissolve the 1-hydroxyanthraquinone. Repeat this operation several times until the barium

hydroxide remains colorless. Decompose the barium salt of alizarin with hydrochloric acid, and recrystallize the alizarin several times from alcohol.<sup>2</sup>

**Analytical reactions.** The first of the hydroxyanthraquinone dyes to be used as an analytical reagent was not alizarin, but the sulfonic acid derivative, sodium alizarinsulfonate, which was first proposed as a reagent for aluminum by Attack in 1915.<sup>1</sup> Both alizarin and sodium alizarinsulfonate, however, have hydroxyl groups in the 1,2-positions, and because of this similarity in structure both compounds react similarly, and serve essentially for the detection and determination of the same substances. Sodium alizarinsulfonate is the more soluble in water, and is perhaps the more frequently used.

Due to its structure, alizarin reacts with many metallic ions to form lakes. The tin, gallium, and aluminum lakes are red, that with calcium is blue, and iron black. Zirconium also reacts with alizarin to give a reddish-violet coloration, and this is changed to a lemon-yellow by the addition of fluorides. Traces of borates change the violet solution of the dye to blue. Other elements which may be detected or determined with the aid of alizarin or sodium alizarinsulfonate are: scandium, thorium, titanium, columbium, indium, uranium, platinum, bismuth, chromium, copper, mercury, and thallium.

For convenience in classifying the information on the analytical uses of alizarin and its sulfonic acid derivative, these two compounds are considered separately in the following sections, although their applications are similar.

**Detection of aluminum:** Aluminum salts react with ammoniacal solutions of alizarin to yield a violet-colored lake, which is probably an inner-complex (page 407). The red compound formed by the action of alizarin on aluminum hydroxide, however, has no definite composition, and appears to be an adsorption product. This reaction is not specific, since many ions give colored solutions or precipitates with alizarin. Bismuth, antimony, cobalt, copper, ferrous, magnesium, mercuric, platinous, and tin salts give red precipitates; cadmium and stannic tin give orange precipitates; ferric iron and titanous black; chromium, yellow; uranium, deep violet; and thallium, dark blue. Soluble compounds or precipitates are also formed with barium, calcium, strontium, zinc, gold, and nickel.<sup>30</sup>

In the absence of interfering ions, however, alizarin may be used for the detection of aluminum.<sup>41,42</sup> Many modifications of this test have been proposed, but the following may be taken as typical:

**Procedure.** To the solution to be tested in a test tube, add 2 drops of a 0.1 per cent solution of alizarin in alcohol and a few drops of concentrated ammonium hydroxide. Shake and let stand 15 minutes. Then add 50 per cent acetic acid until the pH is 5.2; add an equal volume of ether, shake and allow the mixture to stand. A violet color forms at the boundary between the ether and water if as little as 1  $\gamma$  of aluminum is present.<sup>7</sup>

Other tests based on this reaction have been proposed.<sup>8,9,10</sup> Aluminum hydroxide, formed with iron sulfide during the hydrogen sulfide precipitation of the aluminum group, may be separated from the latter by shaking the mixture

with isoamyl alcohol to which alizarin has been added; the aluminum passes into the alcohol layer.<sup>11</sup>

A satisfactory spot test based on the aluminum-alizarin reaction has been proposed by Feigl and Stern.<sup>12</sup>

**Procedure.** Prepare alizarin test paper by moistening filter paper with a saturated alcoholic solution of alizarin and allow to dry. This paper is yellow or yellowish-pink. Place a drop of the solution to be tested on this paper and expose to ammonia. If aluminum is present, the paper turns violet, while the spot appears pink or violet. Dry without heat. The color of the alizarin returns to the paper, but the spot appears a beautiful pink.<sup>12</sup>

As little as 0.15γ of aluminum can be detected at a concentration of only 0.3 mg. of aluminum per liter.

Many ions, such as iron, chromium, uranium, and manganese, interfere by forming colored alizarin lakes, but by employing proper methods this interference can be eliminated. The most satisfactory procedure is based on the fact that aluminum, unlike the other metals of the ammonium sulfide group, forms a soluble compound with potassium ferrocyanide. Thus, when the reaction with alizarin is carried out on paper impregnated with potassium ferrocyanide, those ions forming insoluble ferrocyanides are fixed by precipitation in the paper, while the soluble aluminum compound diffuses to the zone surrounding the precipitate. In this way a satisfactory separation of aluminum from interfering ions is easily accomplished. In making this test, it is best to use small drops so that the amount of ferrocyanide present is adequate to fix the interfering ions. The test is performed as follows:

**Procedure.** Impregnate a piece of filter paper with a saturated solution of potassium ferrocyanide and dry. When a drop of the solution to be tested is placed on this paper, a dark spot surrounded by a bright aqueous ring appears if aluminum is present; and when an alizarin solution is added to the outer zone, and the paper held over ammonia, a rose red ring forms about the inner spot.<sup>13,43</sup>

Feigl advises placing the paper in hot water for two minutes to remove the excess ferrocyanides to make the aluminum lake more visible.

Table 56, taken from the work of Feigl,<sup>14</sup> gives the limits of identification for aluminum in the presence of other metals when the above procedure is used.

TABLE 56.

Aluminum Present	Quantity of Other Ions Present
4.0γ	800γ Iron
3.0γ	300γ Iron + 750γ Chromium
1.4γ	3912γ Manganese
0.6γ	60γ Iron + 372γ Manganese
0.6γ	30γ Iron + 180γ Zinc
0.1γ	30γ Zinc + 20γ Manganese
0.5γ	100γ Uranium
0.6γ	30γ Iron + 72γ Cobalt

Manganese forms a violet lake with alizarin, but any interference from this source may be eliminated by the use of potassium ferrocyanide. Zinc may also be removed in this manner.

With uranium, uranyl ferrocyanide,  $(\text{UO}_2)_2\text{Fe}(\text{CN})_6$ , forms as a slimy precipitate, and tends to diffuse with aluminum. In such cases the uranyl precipitate is dissolved from the paper as  $(\text{NH}_4)_4(\text{UO}_2(\text{CO}_3)_3)$  by soaking the paper, after the test is made, in a solution of ammonium carbonate, or the precipitate may be fixed with a drop of ferric chloride. A separation of the solutions of aluminum and uranium occurs in the capillaries of the paper so that the aluminum and uranium lakes are formed in different zones on the paper. This separation is not satisfactory with metals other than uranium. When a drop of the solution containing both aluminum and uranium is placed on paper impregnated with alizarin, the blue uranium lake forms in the center of the drop while the aluminum diffuses; and, after being developed with ammonia, appears as the red lake surrounding the inner blue spot. The width of the ring is determined by the amount of aluminum present. By this procedure, 0.1% of aluminum can be detected in the presence of 20% of uranium. Aluminum may also be detected in the presence of chromium by a similar procedure.<sup>40</sup>

Cobalt gives a violet color with alizarin, and in the presence of ammonia turns a bluish green. When cobalt is present in the unknown, treat the spot (which has been developed on the test paper with ammonia and then dried) with 0.01 N hydrochloric acid to dissolve the cobalt compound.

If much iron or chromium is present, a control test should be made on an aluminum-free chromium or iron solution; and less confusion is likely to result if, after the addition of alizarin, the ferrocyanide is removed by placing the paper in hot water and then drying. The paper dries white, and thus renders the color of the lake more clearly visible. The control shows little color change.

Aluminum in steel may be detected with alizarin by using a modification of the spot test procedure,<sup>15</sup> and a method for the local microdetermination of aluminum in metals has been proposed.<sup>16</sup> Feigl describes a procedure for detecting aluminum in leather to determine the method of tanning.<sup>17</sup>

**Determination of aluminum.** Alizarinsulfonic acid appears to be a more satisfactory reagent for the determination of aluminum than alizarin, but several quantitative or semi-quantitative methods using alizarin have been described. Most of these methods are more or less unsatisfactory due to interference by other ions. In general, too, it is claimed that alizarin is less satisfactory for the determination of aluminum than aurintricarboxylic acid because of the appearance of a highly colored anion of the dye with increase of the pH of the solution. For this reason the pH of the solution in which the aluminum may be determined is much more restricted with alizarin than with aurintricarboxylic acid.<sup>18</sup>

The semi-quantitative determination of aluminum by a spot method often proves useful. This is carried out as follows: <sup>19</sup>

**Procedure.** Make the solution to be tested alkaline to litmus, with sodium hydroxide, and then place 0.002 ml. of this solution on thin filter paper. Cover with a drop of saturated aqueous ammonium thiocyanate solution mixed with 3 parts of barium nitrate (to eliminate in part interference due to other

cations), and allow to stand 5-10 seconds. Now add 1 drop of alcoholic alizarin, heat carefully to the appearance of a red color, and then wash off the excess of yellow alizarin with alcohol. Compare the color of the spot with that produced by known quantities of aluminum.

By carrying out the spot test on reaction fields of unit area, and employing a technique which permits a uniform distribution of the colored product over the entire surface, a fairly accurate estimation of the quantity of the aluminum originally present may be made.<sup>20</sup> A limitation of the reaction area is easily accomplished by the use of paraffin or similar water repellent. Impregnation of the colored area with paraffin prevents atmospheric disturbance. A comparison of the color is best made by reflected light.

The fluorescent intensity of the reaction between aluminum and alizarin under ultra-violet light in a weakly acid solution has been suggested as a means of estimation of small quantities of aluminum, but this does not appear to be a very satisfactory procedure.<sup>21</sup>

Keilholz has suggested the use of alizarin for the determination of aluminum in plants and human organs.<sup>22</sup>

**Detection of fluorides.** During a study of the metallic derivatives of alizarinsulfonic acid, de Boer<sup>23</sup> found that a red zirconium lake, insoluble in concentrated hydrochloric acid, is formed when alizarinsulfonic acid is added to solutions of zirconium salts, but that in the presence of fluoride ions this reaction fails. Utilizing this interference by the fluoride ion with the formation of the zirconium-alizarin lake, de Boer suggested that this might constitute a sensitive test for the fluoride ion. The test which has been developed using this principle depends upon the fact that the red-violet color of the zirconium-alizarin lake turns yellow in the presence of even traces of fluoride ion.<sup>24-27</sup>

Stone has found that alizarin is a more sensitive reagent than alizarinsulfonic acid, and is less likely to react with interfering substances.<sup>25</sup> The test using alizarin is carried out as follows:

**Reagent.** *Alizarin solution:* Dissolve 0.5 g. of alizarin in 200 ml. of alcohol.

*Zirconium solution:* Dissolve 1.5 g. of zirconium chloride in 75 ml. of alcohol.

Mix these two solutions and allow the precipitated lake to settle. Filter, wash 2 times with alcohol, and then suspend the moist precipitate in sufficient alcohol to make the total volume 25 ml. Shake well and add 5 ml. of this suspension to 100 ml. of water. This is the reagent. It must be well shaken before use.

**Procedure.** To 2.5 ml. of the solution to be tested, add an equal volume of concentrated hydrochloric acid and 0.5 ml. of the reagent. The red color turns yellow almost immediately if the solution contains more than 0.3 mg. of fluoride. The solution is decolorized after 15 seconds with 0.03 mg. of fluoride. This is the practical limit of the test, but the reaction may be made somewhat more sensitive by using less reagent and allowing the mixture to stand longer.

Phosphate, sulfate, and oxalate decolorize the reagent; and oxidizing agents, such as chlorate, iodate, and bromate, which oxidize the chloride ion to free chlorine, interfere by bleaching the reagent. This interference may be eliminated by the addition of sodium sulfite.

A spot test may also be used to detect fluoride by this reaction.<sup>24,25,38</sup>

**Reagent.** Add about 70 mg. of  $ZrO_2$  to 100 ml. of dilute hydrochloric acid and warm. Filter if necessary, and treat this solution with a slight excess of alcoholic alizarin solution. The excess of alizarin is detected by the yellow color which appears in the ether layer obtained when a few ml. of the reagent are shaken with a little ether and allowed to stand. Warm the zirconium-alizarin solution 10 minutes on a water bath, and then impregnate filter paper with this solution and dry.

**Procedure.** Moisten a strip of the dried paper with a drop of 50 per cent acetic acid, and then place on the moist spot a drop of the neutral solution to be tested. A yellow spot appears if fluorides are present. If a positive test is not obtained immediately, hasten the reaction by warming in steam.

By the above procedure, 1 $\gamma$  of fluoride may be detected at a concentration of 1:50,000. Arsenate, sulfate, oxalate, and phosphate interfere and must be removed before making the test. Oxalates may be removed by ignition. Interference due to sulfate is eliminated by adding a drop of benzidine hydrochloride to the solution to be tested, and then placing a drop of the benzidine sulfate suspension on the paper. The yellow color due to fluoride may be observed by turning to the reverse side of the paper.

**Determination of fluoride.** Alizarinsulfonic acid is generally used instead of alizarin for the determination of fluorides, although the latter gives similar reactions. For the details of fluoride determination, refer to the section on alizarinsulfonic acid (page 427).

**Detection of uranium.** Uranium may be detected by a spot test procedure similar to that employed for aluminum. When the alizarin paper is treated with a drop of neutral or weakly acid solution to be tested a clear blue color is obtained. Development of the spot in ammonia is necessary only if the solution is acid. The reaction is sensitive to one drop containing 0.0052 mg. of uranium.<sup>12,42</sup>

**Determination of sodium.** Sodium may be determined indirectly after precipitating with magnesium uranyl acetate by determining the uranium content of the precipitate colorimetrically with the aid of alizarin.<sup>46</sup>

**Reagents.** *Magnesium uranyl acetate reagent:* Dissolve 32 g. of uranyl acetate, 100 g. of magnesium acetate, and 20 ml. of glacial acetic acid in 300 ml. of water. When the solid is completely dissolved, cool, and dilute to 1 liter. Allow to stand 48 hours, filter, and keep in a dark place.

*Alizarin solution:* Dissolve 2 g. of alizarin in 1 liter of 95 per cent alcohol. Let stand 24 hours at 40° C., and filter.

**Procedure.** For 100-400 $\gamma$  of sodium, carry out the precipitation in a fritted glass crucible as follows: pour in approximately 0.5 ml. of the solution to be analyzed, and then add 1.5 ml. of the magnesium uranyl acetate reagent. Allow to stand 30 minutes, filter with suction, and wash with the precipitating solution. Then wash 3 times with 1-ml. portions of alcohol saturated with the precipitate. Transfer the crucible to a 100-ml. measuring flask arranged for suction. Add 1 ml. of distilled water, and allow to stand a short time. Then apply suction, and filter the solution into the flask. Repeat this treatment with fresh portions of water until the precipitate is completely dissolved. Dilute the filtrate to 90 ml. and add 7 ml. of the alcoholic alizarin solution, and then dilute to 100 ml. with water. Determine the extinction coefficient of the solution with a Pulfrich Photometer (filter S57, 0.5 cm. cuvette) within 1 hour of the time of addition of the alizarin solution.

For the comparison solution, use 7 ml. of the alizarin reagent, 40 ml. of 95 per cent alcohol, and dilute to 100 ml. This solution is stable.

When the extinction coefficient is plotted against  $\gamma$  of sodium, a straight line is obtained, but this does not pass through the origin. The mean absolute error using the above method is 4 $\gamma$  of sodium.

For the determination of 25-150 $\gamma$  of sodium, proceed as described above, but in this case use only 4 ml. of alizarin. The comparison solution should contain only 30 ml. of alcohol. Use a 2-cm. cuvette. The mean absolute error is 2.5 $\gamma$  of sodium.

The method is satisfactory when applied to deproteinized blood serum. Heavy metals, potassium, and phosphate do not interfere.

**Detection of zirconium, titanium and thorium.** Zirconium salts in an acid solution give a reddish-brown to violet precipitate with an alcoholic solution of alizarin. The zirconium-alizarin compound forms more quickly on warming. Its composition is unknown. Other hydroxyanthraquinone dyes give similar reactions. The zirconium test is performed as follows: <sup>28</sup>

**Reagent.** Treat an alcoholic solution of commercial alizarin dropwise with dilute hydrochloric acid until a pure yellow color is obtained, and then add an equal volume of alcohol and filter.

**Procedure.** Make the solution to be tested as nearly neutral as possible, and mix one drop of this solution with one drop of the alizarin solution and boil immediately. In the presence of zirconium, beryllium, aluminum, titanium, and thorium salts a red to violet color appears. Now add 1 drop of dilute hydrochloric acid. The zirconium compound alone remains unaffected, and consequently may be detected in the presence of the above metals.

If zirconium is present in considerable concentration, a red to violet color or precipitate may form, but with low concentrations only red-brown flecks appear. In this way 0.5 $\gamma$  zirconium may be detected at a concentration of 1:100,000. The presence of much aluminum or thorium causes a decrease in the sensitiveness of the reaction. Fluorides, sulfates, phosphates, organic hydroxy acids, molybdates, and tungstates interfere, since their radicals reduce the zir-

conium ion concentration by precipitation or by complex ion formation. Sulfates may be removed by the addition of barium chloride.

Titanium, zirconium, and thorium are detected by means of a spot test using alizarin.<sup>29</sup>

**Procedure.** Place a drop of the solution to be tested on a strip of filter paper that has been soaked in an alcoholic alizarin solution and dried, and then hold over ammonia fumes. The spot becomes colored if thorium, zirconium, or titanium is present. Thorium gives a violet color; zirconium a raspberry-red color; and titanium a reddish-violet color.

The following sensitivities are reported:

Thorium	0.24 $\gamma$ at a dilution of 1:125,000
Zirconium	0.29 $\gamma$ at a dilution of 1:103,000
Titanium	0.18 $\gamma$ at a dilution of 1:166,000

Tartaric acid and other substances which prevent the precipitation of metallic hydroxides by ammonia interfere.

**Determination of zirconium.** The lake formed in the reaction between alizarin and zirconium may be used for the colorimetric determination of the latter. The color follows Beer's law rather closely up to 4 p.p.m. of zirconium. The alizarin lake eventually settles out, but it is redispersed by shaking, and the transmission curve of such a suspension differs but very little from one that is freshly prepared.

The final acidity of the solution affects the color intensity considerably. For example, with 50 $\gamma$  of zirconium under conditions described in the procedure below, the minimum transmittancy at 560  $m\mu$  is obtained with 0.05 ml. of 12 N hydrochloric or perchloric acid in excess. When there is no acid, or 0.5 ml. in excess, there is an increase in transmission corresponding in both cases to -4.2 $\gamma$ . With 1 ml. of acid in excess the error is increased to -11.6 $\gamma$ .<sup>46</sup>

Complex-forming substances, such as fluorides, sulfates, phosphates and organic hydroxy acids destroy the color of the zirconium compound. Molybdates and tungstates have a similar effect. Ferric, chromic and cobalt ions cause positive errors, and cadmium, copper, lead and aluminum cause negative errors. This effect is more pronounced in hydrochloric acid than in perchloric acid solutions. Titanium also forms a lake with alizarin, even in fairly strongly acid solutions, and this causes high results in the zirconium determination. The thorium lake does not form easily in the presence of sufficient hydrochloric acid (2 ml. 12 N hydrochloric acid in 25 ml.). Hafnium gives the same color reaction as zirconium.

The transmission curves of the lakes of the two elements are qualitatively identical. One g. of zirconium is spectrophotometrically equivalent on the average to 2.55 g. of hafnium. Consequently, in a known weight of a mixture of these two elements, containing no other elements, it is possible to determine each indirectly, provided the ratio is not too unfavorable.

**Reagents.** *Alizarin solution;* Dissolve 0.125 g. of alizarin in 100 ml. of ethyl alcohol.



**Standard zirconium solution:** Dilute a 0.1-0.2 per cent solution of zirconium in 4 N hydrochloric acid to form a 0.01 per cent zirconium solution in 2 N hydrochloric acid. This stock solution is standardized by precipitating with ammonia and igniting the precipitate to zirconium oxide.

**Procedure.** Transfer 1 ml. or less of the zirconium solution, which should contain 5-100 $\gamma$  of zirconium in approximately 2 N hydrochloric acid, to a 25-ml. volumetric flask that has been thoroughly rinsed with alcohol. Add 0.50 ml. of the alizarin solution, and then make the mixture slightly alkaline by the dropwise addition of ammonium hydroxide. Allow the mixture to stand 2 minutes, neutralize with 1 N hydrochloric acid, and add 0.10 ml. of 7 N hydrochloric acid. Dilute the mixture to 25 ml. with alcohol, and read the color in a photometer, using a wave-length of 560 m $\mu$ .

**Detection of indium.** Alizarin forms with indium a dark red lake, which may be used as a test for this metal. The test is not specific, since a large number of metals form similar lakes, but if conditions are carefully controlled, indium can be detected in the presence of aluminum, nickel, cobalt, manganese, zinc, iron, and chromium, provided the concentration of the latter is not too great.<sup>30</sup>

**Procedure.** Soak a piece of filter paper in a saturated alcoholic solution of alizarin; and, when dry, apply a drop of the solution to be tested, which must be neutral or only slightly acid with acetic acid. Develop the spot over ammonia, and then immerse in a saturated aqueous solution of boric acid. The violet ammonium alizarinate is decomposed by the acid, and the red indium lake becomes visible against the yellow background. In this way 0.05 $\gamma$  of indium may be detected at a concentration of 1:500,000.

Interference by iron may be eliminated by placing a drop of the solution to be tested in a small porcelain dish, and adding a concentrated solution of sodium thiosulfate dropwise until no further violet coloration is produced. Then add a crystal of sodium sulfite and finally 6-8 drops of 5 per cent potassium cyanide solution, which should be sufficient to dissolve any precipitate when the mixture is heated. Use this solution and proceed with the test as above, using impregnated alizarin paper and boric acid. By this treatment 1 $\gamma$  of indium can be detected in the presence of 450 $\gamma$  of iron.

Aluminum, which also interferes with the indium test, forms the complex ion  $(\text{AlF}_6)^{-3}$ , with soluble fluorides, and so may be rendered harmless by the addition of sodium fluoride. Thorium, zirconium, and beryllium, which also interfere, either form precipitates or complexes with sodium fluoride, and so probably may be removed by this treatment. After the addition of sodium fluoride, 1 $\gamma$  of indium can be detected in the presence of 375 $\gamma$  of aluminum.

Manganese, cobalt, zinc, and nickel form with alizarin colored lakes which are stable to boric acid under the conditions of the test. Since these four ions are converted to complex cyanide ions with soluble cyanides, any interference from this source may be removed by adding 1 drop of 5 per cent potassium cyanide solution to the test paper, then adding a drop of the unknown, and then another drop of potassium cyanide solution. This treatment is then followed by the regular procedure with ammonia and boric acid.

By following the above procedure, the following sensitivities may be obtained:

0.13  $\gamma$  indium may be detected in the presence of 2200 times as much zinc. The concentration limit is 1:192,000.

0.6  $\gamma$  indium may be detected in the presence of 550 times as much manganese. The concentration limit is 1:40,000.

0.1  $\gamma$  indium may be detected in the presence of 2,400 times as much cobalt. The concentration limit is 1:250,000.

0.06  $\gamma$  indium may be detected in the presence of 5,900 times as much nickel. The concentration limit is 1:400,000.

If chromium is present with indium, convert to the chromite, which does not react with alizarin, by substituting 0.5 N sodium hydroxide for potassium cyanide in the above procedure. In the presence of 800 times as much chromium, 0.6 $\gamma$  of indium can be detected. The concentration limit is 1:40,000.

**Detection of mercury.** An indirect test for mercury has been devised using alizarin. Aluminum amalgam, which is formed when mercury or solutions of mercury salts are brought into contact with aluminum, is quickly converted to aluminum oxide in contact with moist air. This activity is in marked contrast to the stability of pure aluminum. The mercury which is liberated when the aluminum oxide is formed is free to amalgamate with additional aluminum, and this procedure is continued so that small quantities of mercury may be detected by the formation of aluminum oxide.<sup>31,32</sup> One of the most satisfactory methods for carrying out this test involves the electrolytic precipitation of mercury on aluminum foil, followed by the identification of the small amount of aluminum oxide by the lake which it forms with alizarin.<sup>33</sup>

When using alizarin for this test, the electrolysis must be carried out in neutral solution, since both alkali and acid solutions react sufficiently with metallic aluminum to give a pronounced reaction with the alizarin solution even if mercury is not present. When it is possible to make the test in a neutral solution, the mercury is best deposited directly on the aluminum cathode, and the aluminum oxide detected *in situ* by applying an acetic acid solution of the alizarin to the metal. In an acid or alkaline solution, however, the mercury must be deposited on a platinum cathode, which is then washed with water and made anode against a cathode of aluminum foil. During electrolysis the mercury dissolves from the platinum anode and is reprecipitated on the aluminum with the results above stated. For the complete details of this test, refer to the original reference.<sup>33</sup> In a neutral solution as little as 0.0001 $\gamma$  mercury can be detected in a solution at a dilution of 1:500,000,000. The sensitiveness is somewhat less in acid solutions.

**Detection of gallium.** Gallium may be detected by the formation of a light red lake with alizarin.<sup>34</sup> This test, however, like so many others using alizarin, is seriously influenced by the presence of other ions. For this reason

the test should be applied only after the separation of gallium from all interfering ions. The method of separation recommended is to extract the hydrochloric acid solution of gallium chloride with ether according to the procedure of Swift;<sup>84</sup> and, after removal of the ether, to precipitate the gallium from a solution alkaline to phenolphthalein with a 5 per cent solution of 8-hydroxyquinoline in alcohol. The precipitate is then dissolved in hydrochloric acid, and gallium detected with alizarin, using the spot method. According to Wenger and Duckert, however, this test is not sufficiently sensitive to be of great value.<sup>85</sup> Morin and quinalizarin are recommended as the most satisfactory reagents for gallium.

**Determination of calcium.** Laidlaw and Payne<sup>86</sup> have developed a method for determining calcium in blood, which is suitable for quantities of calcium ranging from 0.1 mg. to 0.002 mg. Calcium is precipitated as the oxalate, which is then dissolved and reprecipitated as calcium alizarinate with alcoholic alizarin. The precipitate is washed, decomposed with oxalic acid in 50 per cent alcohol, and the alizarin which is set free is dissolved in 95 per cent alcohol. This solution is then made just alkaline with ammonium hydroxide, and the alizarin estimated colorimetrically by comparison with standard solutions of ammonium alizarinate. The calcium in the alizarinate is only one-sixth the weight of the alizarin, and so the initial weight of the calcium in blood is obtained by dividing the weight of alizarin found by 6. Since 0.001 per cent alizarin is used, the method is very sensitive.

**Reagents.** *Alizarin reagent:* Dissolve 0.1 g. of pure alizarin in 100 g. of 95 per cent alcohol.

*Standard alizarin solution:* Prepare an accurately measured 0.001 M solution of pure alizarin in 95 per cent alcohol. Transfer 2 ml. of this solution to a 50-ml. volumetric flask, add 1 ml. of a concentrated solution of oxalic acid in 50 per cent alcohol, and then add a volume of 95 per cent alcohol which is equal to the volume used in extracting the alizarin from the Gooch filter in the procedure of analysis. Add a little water, make just alkaline with ammonia, dilute to the mark and mix thoroughly.

**Procedure.** Ignite the sample containing a few tenths milligram of calcium, and dissolve the ash in 0.5 ml. of N hydrochloric acid. Transfer to a centrifuge tube with the aid of 2 ml. of wash water, and then add 1 ml. of a saturated solution of ammonium oxalate, 2 ml. of a saturated solution of calcium-free sodium acetate, and mix thoroughly. Allow to stand for at least 3 hours and centrifuge for 2 minutes at 4000 r.p.m. Remove the supernatant liquid as completely as possible with a pipet without disturbing the precipitate, and add 3 ml. of a 0.1 per cent solution of ammonium oxalate. Stir the precipitate, and centrifuge immediately. Remove the supernatant liquid as before, and dissolve the calcium oxalate in 0.5 ml. of N hydrochloric acid. Transfer the solution to a test tube, and wash out the centrifuge tube 4 or 5 times with water. The total volume of the solution and washings in the test tube should be between 8 and 10 ml. Add an excess of the alizarin reagent, warm the solution on a

water-bath to about 80° C., add 5 drops of concentrated ammonium hydroxide solution and mix. Use 1 ml. of the alizarin solution for each 0.1 mg. of calcium. Keep the purple mixture warm for about 1 hour, and allow to stand overnight. Calcium is precipitated as blue-black microcrystalline needles of calcium alizarinate.

Filter the precipitate of calcium alizarinate on a Gooch filter of fine asbestos, using gentle suction. Wash the precipitate with dilute ammonium hydroxide solution. Now place the test tube in which the crystallization took place under the delivery from the Gooch crucible, and pour over the precipitate 1 ml. of a concentrated solution of oxalic acid in 50 per cent alcohol. Be sure and pour the alcoholic oxalic solution over every part of the filter. The blue-black calcium alizarinate is immediately decomposed to yield an orange color of free alizarin. Wash the alizarin through the filter with warm 95 per cent alcohol into the test tube, and then transfer the alizarin solution to a 50-ml. volumetric flask. Wash out the test tube with dilute ammonium hydroxide. Make the solution just alkaline with ammonia and dilute to the mark with water. Mix thoroughly and transfer to a colorimeter and compare against the standard solution of ammonium alizarinate. Determine the quantity of alizarin in the sample from height of the column of solution which matches the standard, and this figure when divided by 6 gives the weight of calcium in the sample.

**Detection of copper.** Alizarin reacts with solutions of cupric salts to give a light red precipitate. This may be used for the detection of small quantities of copper.<sup>44,45</sup>

**Detection of columbium.** A flocculent red precipitate is obtained when a half-saturated solution of alcoholic alizarin is added to an acetic acid solution containing sodium acetate and trivalent columbium.<sup>87</sup> The lake may be an adsorption complex, but is perhaps a chelate compound similar to that formed when aluminum salts react with alizarin.

**Procedure.** To make the test, add 1 ml. of 2 N acetic acid, 1 ml. saturated sodium acetate, and 1 ml. half saturated alcoholic alizarin to a 2 N sulfuric acid solution containing trivalent columbium. Heat a short time, cool, and after one hour note the appearance of the mixture. A red flocculent precipitate is a positive test for columbium. As little as 25γ of the metal may be detected by this method.

**Detection of ammonia.** When exposed to ammonia gas, moist alizarin paper turns purple, and upon drying the ammonia escapes and the yellow color of alizarin returns. This color reaction has been used by Frings<sup>47</sup> for the detection of ammonium salts, which are converted to ammonia by the action of a base.

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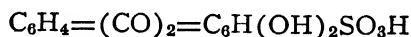
**ALIZARINSULFONIC ACID**

Synonym : 1,2-Dihydroxyanthraquinone-3-sulfonic acid, alizarin red, alizarin red S, sulfoalizarin

$C_{14}H_8O_7S$

Mol. Wt. 320.26

Beil. Ref. XI, 355.



**Use:** Detection of aluminum, barium, beryllium, bismuth, boron, calcium, chromium, copper, fluorine, hafnium, iron, lead, lithium, mercury, platinum, potassium, scandium, thallium, thorium, tin, titanium, uranium and zirconium.

Determination of aluminum, boron and fluoride.

Alizarinsulfonic acid is an orange-yellow crystalline compound. It is soluble in water and ethyl alcohol, but is insoluble in ether.

**Preparation:** Heat alizarin for several hours at 100-150° C. With 3 parts of fuming sulfuric acid (20 per cent  $SO_3$ ) until the product is soluble in water. Pour the mixture into water and neutralize with calcium hydroxide. Convert the calcium salt to the sodium salt with sodium carbonate and filter. Evaporate the solution to dryness.

The free acid can be salted out of solution. Alizarin-3-sulfonic acid can be separated from the small quantity of alizarin-4-sulfonic acid which is also formed by dissolving the former in alcohol.<sup>1</sup>

**Analytical reactions.** The sulfonic acid group of alizarinsulfonic acid does not function as a part of the reactive structure of the molecule, but seemingly serves only to increase the solubility of the compound. With the exception of the sulfonic acid group, the remainder of the molecule is identical with that of alizarin, and accordingly there is little difference in the analytical behavior of these two compounds.

**Detection of aluminum.** Aluminum salts give a red precipitate with alizarinsulfonic acid in an ammoniacal solution. The red compound is probably an inner-complex salt corresponding in composition to the corresponding alizarin compound. The aluminum lake is stable to dilute acetic acid, while the violet color of the excess alizarinsulfonic acid is destroyed upon acidifying, since acid solutions of the dye are pale yellow in color.

A simple test for aluminum is carried out as follows:<sup>2</sup>

**Procedure.** To about 5 ml. of a neutral or acid solution to be tested, add 1 ml. of 0.1 per cent alizarinsulfonic acid solution (sodium salt), and then add ammonium hydroxide until the mixture is alkaline. Boil for a few minutes, allow to cool, and then acidify with dilute acetic acid. A red color or precipitate indicates the presence of aluminum.

This reaction will detect 1 part of aluminum in 10 million parts of water. This test is suitable for the detection of aluminum in a scheme of analysis.<sup>74</sup> Salts of calcium, strontium, barium, magnesium, zinc, and all other metals later than group II do not interfere. If cobalt is present, an excess of ammonium

hydroxide must be avoided. Phosphate and chromium do not interfere, nor does iron unless present in comparatively large quantity. Citric acid may be used to keep larger quantities of iron in solution. Fluorides also interfere by forming the aluminum complex,  $\text{AlF}_6^{-3}$ .<sup>3</sup>

It is not generally a good plan to attempt the separation of aluminum as the hydroxide before making the test, since most samples of sodium peroxide, sodium hydroxide and hydrogen peroxide used for this purpose contain sufficient aluminum to give the test.

A modification of the above test has been proposed by Korenman.<sup>4</sup>

**Procedure.** To 2-3 ml. of the sample, add ammonium chloride and 2 N ammonium hydroxide until a noticeable odor of ammonia is observed. Heat to boiling, filter, and wash the precipitate of aluminum hydroxide with 2 N ammonium hydroxide containing ammonium chloride. Then digest the residue with 2 N ammonium hydroxide, filter, and mix 2-3 ml. of the filtrate with an equal volume of concentrated ammonium chloride, and finally add 1-2 drops of an aqueous solution of sodium alizarinsulfonate. A red color appears if aluminum is present, but in its absence the solution is violet.

The following ions do not interfere: magnesium, calcium, strontium, barium, ferric, chromic, manganese, zinc, cobalt, nickel, mercuric, lead, bismuth, copper, cadmium, arsenic, antimony, stannous, silver phosphate, borate, fluoride, silicate, and oxalate.

A somewhat different aluminum test is performed as follows:<sup>5</sup>

**Reagent.** Mix 10 ml. of 0.4 per cent zirconium nitrate,  $\text{ZrO}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , solution with 5 ml. of a 0.4 per cent alcoholic solution of sodium alizarinsulfonate and 1 ml. of about 0.6 N potassium fluoride solution, and then dilute to 65 ml. with 2 N hydrochloric acid.

**Procedure.** Heat about 1 ml. of the solution to be tested (having an acid concentration not greater than 0.25-0.5 N hydrochloric acid) to boiling in a test tube, and mix with an equal volume of the reagent. Heat to boiling, and cool in a stream of cold water. If aluminum is absent, the solution becomes yellow or golden-yellow in color, but if aluminum is present, the color is crimson.

For concentrations of aluminum up to 0.01-0.02 N the intensity of the coloration is proportional to the aluminum content.

The sensitivity of the reaction is determined by the concentration of the fluoride ion. By following the above procedure, 1 part of aluminum in 500,000 parts of solution can be detected. For the detection of aluminum at concentrations below 0.01 N, a blank test should be made. The method is rapid, and reliable for detecting aluminum in a mixture of cations of group III after group IV has been removed. Sulfate, fluoride, hypochlorite, and oxalate interfere, but interference from these sources may be eliminated by precipitating the aluminum with sodium or potassium carbonate, and then testing the residue for aluminum.

**Determination of aluminum.** The color produced in the reaction between sodium alizarinsulfonate and solutions of aluminum salts was first used

by Atack for the colorimetric estimation of small quantities of aluminum.<sup>2</sup> This method, modified from time to time by various investigators,<sup>8-9</sup> has proved useful for determining aluminum in various materials, although it is subject to many inaccuracies unless all conditions are properly controlled. The color intensity of a solution containing aluminum and alizarinsulfonic acid depends to such an extent upon such variable factors as the amount of aluminum-alizarin lake; the ratio of aluminum to alizarinsulfonic acid; the hydrogen ion concentration; time of addition of the acid; and presence of interfering substances, that it has been rather difficult to establish a satisfactory general procedure. It may be noted here that the temperature effect is very slight.

After studying the factors affecting the results obtained in determining aluminum colorimetrically by the Atack method, Musakin proposed the following procedure:<sup>10</sup>

**Procedure.** To a neutral or slightly acid solution of aluminum, containing 0.03-0.003 mg. of the metal, add 5 ml. of 0.05 per cent solution of sodium alizarinsulfonate and 5 ml. of a saturated solution of sodium chloride, and then add dropwise 5 N ammonium hydroxide (freshly distilled) to the first change of color and then dilute to 50 ml. Next prepare a solution which contains the same quantities of the alizarinsulfonic acid reagent, hydrochloric acid, ammonium hydroxide and sodium chloride, and titrate with a standard solution of aluminum until the color is similar to that of the unknown. Then dilute to 50 ml., allow to stand 5 minutes, and carefully acidify both unknown and standard solutions with equal volumes of acetic acid to a permanent orange color. Add a few more drops of acetic acid, dilute if necessary, and compare in a colorimeter. To prepare the standard aluminum solution, dissolve 1.3334 g. of aluminum chloride in 950 ml. of distilled water and dilute to 1 liter.

Small quantities of sulfide, nitrate, and stannic tin do not interfere, but copper, iron, chromium, cobalt and manganese must be absent. There must be no excess of hydrochloric acid, ammonium chloride, ammonium hydroxide, or acetic acid, and citric acid must not be used.

The intensity of the coloration is a function, not only of the quantity of the aluminum-alizarin lake, but also of other factors, such as the pH of the medium at the time of lake formation and after the addition of acetic acid, the time of addition of the acetic acid, the amount of alizarinsulfonic acid used, and the presence of interfering substances. Further, the ratio between the color intensity and the aluminum content of the solution is effective only within the rather narrow limits of  $\pm 10$  per cent of the correlations of the concentrations of the standard and tested solutions. Iron, even when present only in traces, seriously affects the determination; and the effect of this ion cannot be eliminated by the use of citric acid.<sup>11</sup>

Musakin<sup>12</sup> has studied the intensity curves for the aluminum-alizarin lake at varying pH, and the most favorable hydrogen ion concentration was found to be at pH 3.6. The results of these studies also show that the depth of color produced does not obey Beer's law, since the concentration of alizarinsulfonic



acid affects the color of the solution somewhat. The error due to this effect may be eliminated by the use of the following equation, proposed by Musakin<sup>13</sup>

$$(C_1 + a)h_1 = (C_2 + a)h_2$$

where

c = concentration of the aluminum ion

a = concentration of alizarinsulfonic acid (= 0.025 if 5 ml. of 0.1 per cent reagent is used)

h = intensity

In concentrated solutions of aluminum, the lake appears to be, at least in part, an adsorption complex of varying composition; and the composition depends somewhat on the pH of the medium in which the compound is formed.<sup>14</sup> Thus, pH becomes an important factor in aluminum determination by this method.

The interference due to ferric ion may be removed by extracting the solution to be determined with a mixture of 32 per cent potassium thiocyanate and 1:1 amyl alcohol. Ferric thiocyanate is quite soluble in amyl alcohol and is removed.<sup>13</sup>

Thrun<sup>9</sup> suggests the use of a starch glycerite solution to prevent the precipitation of the aluminum-alizarin lake.

Savchenko<sup>15</sup> has used alizarinsulfonic acid for the determination of aluminum in glass, and Okhotin and Zubareva<sup>16</sup> have used the same reagent for the determination of aluminum oxide in metallic aluminum. Schams<sup>73</sup> has used a similar procedure for the determination of aluminum in plants. Haywood and co-workers<sup>79</sup> have used alizarinsulfonic acid for the determination of aluminum in magnesium alloys containing up to 12 per cent aluminum.

Egriwe<sup>17</sup> has studied the methods for determining aluminum using alizarin-sulfonic acid, morin, alizarin red PS, and eriochromcyanin R, and has found that while alizarinsulfonic acid is the most sensitive, it is also the most sensitive to the disturbing effect of iron. Eriochromcyanin R is perhaps the most satisfactory of the four dyes studied in the presence of iron.

**Detection of fluoride.** Solutions of zirconium compounds in hydrochloric acid are colored a deep reddish-violet by alizarinsulfonic acid due to the formation of a zirconium-alizarin lake. Solutions containing the lake, however, immediately turn yellow on the addition of an excess of fluoride, since with fluoride the zirconium forms the stable complex ion,  $ZrF_6^{-3}$ , leaving only the yellow color of the liberated alizarinsulfonic acid.<sup>18</sup> This reaction has been made the basis for a very sensitive test for fluoride. The procedure is similar to that using alizarin (page 414). The following reagent gives satisfactory results:<sup>19</sup>

**Reagent.** Dissolve 0.02 g. of zirconium as  $ZrOCl_2$  and 0.015 g. sodium alizarinsulfonate in 10 ml. of water and 60 ml. of concentrated hydrochloric acid.

This violet solution is colored yellow by the addition of as little as 0.001 mg. of fluoride per ml.<sup>19,20</sup> Fluorine in complex fluorides, such as  $AlF_6^{-3}$ ,  $SiF_6^{-2}$ , and  $BF_4^{-}$ , and the fluoride ion behave similarly.

A number of anions, such as sulfate, thiosulfate, phosphate, oxalate, and arsenate either precipitate zirconium or form complex ions with it, and so react in the same manner as fluorides. For this reason these ions must be absent while making the fluoride test.<sup>21,22</sup> Aluminum, yttrium, cerium, erbium, thallium, columbium, tungsten, titanium, thorium, molybdenum and uranium, like zirconium, yield violet colorations with alizarinsulfonic acid; but unlike zirconium, the color formed when alizarinsulfonic acid is added to solutions of these ions is discharged when the solutions are acidified with concentrated hydrochloric acid. Hence, if the fluoride test is carried out in a hydrochloric acid solution, the above cations do not interfere.<sup>18</sup>

Considerably more fluoride (sometimes four times as much as stated by de Boer) is necessary to change the color of the zirconium-alizarin lake in the complete absence of hydrochloric acid, and this amount becomes less as the quantity of hydrochloric acid becomes greater. The color change occurs in the total absence of fluoride when the concentration of the hydrochloric acid is 8.45 N. Similarly, 0.001 N hydrofluoric acid, 0.16 N phosphoric acid, 4.1 N sulfuric acid, and 10.5 N hydrobromic acid cause this change.<sup>23</sup>

The fluoride reaction is perhaps best carried out as a spot test, using paper impregnated with a zirconium-alizarin lake.<sup>24</sup>

**Reagent.** Dissolve 0.25 g. of zirconium nitrate,  $\text{Zr}(\text{NO}_3)_4$ , in 60 ml. of water and mix with a filtered solution of 0.15 g. sodium alizarinsulfonate in 40 ml. of alcohol. Immerse strips of ashless filter paper in this mixture and dry.

**Procedure.** Moisten the test paper with dilute hydrochloric acid, and then apply a drop of solution to be tested. A yellow spot appears if fluorides are present.

Biltz<sup>25</sup> recommends the following reagent for detecting larger quantities of fluorides.

**Reagent.** Impregnate filter paper with a 5 per cent solution of zirconium nitrate,  $\text{Zr}(\text{NO}_3)_4$ , in 5 per cent hydrochloric acid; and, after drying, immerse in a 2 per cent aqueous solution of sodium alizarinsulfonate. Wash the paper with water until the wash water is almost colorless and then dry.

Alimarin<sup>21</sup> has used alizarinsulfonic acid to detect fluorides in silicates and rocks, and Feigl<sup>26</sup> has proposed a spot test to detect fluorides in insoluble fluorides.

**Determination of fluoride.** Small quantities of fluoride may be determined with reasonable accuracy with the aid of alizarinsulfonic acid.<sup>19,27</sup> So many factors affect the accuracy of this method, however, that satisfactory results are obtained only by careful attention to details of procedure. Several different methods have been used based on the effect of fluorides on the color of the zirconium-alizarin lake, or on the formation of a lake by a titration technique employing solutions either of zirconium or thorium salts as titrants and sodium alizarinsulfonate as the indicator.

For the determination of very small quantities of fluorides in water, plants, and minerals, colorimetric methods have proved reasonably satisfactory. Such methods are based upon the fact that solutions of zirconium salts, whether nitrate or oxychloride, and sodium alizarinsulfonate form a red lake, which is stable in acid solutions; and that the colored lake fades in the presence of fluorides due to the removal of zirconium as the complex ion,  $\text{ZrF}_6^{-2}$ . This produces a series of colors ranging from pink to yellow-green. Since under strictly controlled conditions, the depth of color of the solution is dependent upon the amount of zirconium present, the concentration of fluoride may be determined from the fading of the lake by comparison with standard solutions containing known quantities of fluoride.

Many of the early procedures for the determination of fluorides in water have proved unreliable due to interference by sulfates and to the alkalinity of the sample. When the color of the lake is developed with hydrochloric acid, the effect of sulfates in the sample must be considered. Interference from this source has been found less if the solutions are acidified with both hydrochloric and sulfuric acids rather than with hydrochloric acid alone. According to Walker and Findlay,<sup>67</sup> however, when the concentration of sulfate exceeds 120 parts per million, the colorimetric determination of fluoride by means of the zirconium-alizarin lake is unsatisfactory, even though both hydrochloric acid and sulfuric acids are used. By the use of sulfuric acid alone, Lamar and Seegmiller<sup>28</sup> report that waters containing up to 500 parts per million of sulfate may be successfully analyzed for fluoride without the use of a correction curve.

The presence of bicarbonates or other basic substances may affect the pH of the solution to such an extent as to interfere with the fluoride determination, although 1000 p.p.m. of bicarbonate may be present without appreciable effect if fairly concentrated hydrochloric acid is used.<sup>29</sup> The bicarbonate should be neutralized if in concentrations greater than 150 p.p.m. in methods using hydrochloric and sulfuric acids at a lower concentration. According to Lamar and Seegmiller,<sup>28</sup> however, the use of nitric acid to neutralize alkalinity eliminates any uncertainty from that source. Interference due to chloride and nitrate has been studied by Bowes and Murray.<sup>41</sup>

The following method for the determination of fluoride in water gives satisfactory results:<sup>28</sup>

**Reagent.** Dissolve 1.75 g. of  $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  in 250 ml. of water. Prepare a second solution by dissolving 0.35 g. sodium alizarinsulfonate in 250 ml. of water. When ready to use, add 10 ml. of the zirconyl nitrate solution to approximately 50 ml. of distilled water, and then add slowly with constant stirring 10 ml. of the alizarinsulfonate solution and dilute the mixture to 200 ml. with distilled water. Store in the dark, and do not use after two or three days.

**Procedure.** Place 100 ml. of the clear solution to be analyzed in a comparison tube, neutralize the alkalinity with 0.1639 N nitric acid (this is not necessary if the bicarbonate concentration is less than 100 p.p.m.), dilute to 105 ml., and add exactly 5 ml. of 2.1 N sulfuric acid. Prepare a series of standard fluoride solutions by transferring 0, 2, 4, 6, 8, 10, and 12-ml. portions of a stock solution containing 0.2210 g. of sodium fluoride per liter to a series

of comparison tubes. One ml. of the sodium fluoride solution contains 0.01 mg. of fluoride ion. Make up the volume of each to 105 ml., and add exactly 5 ml. of 2.1 N sulfuric acid. Add 5 ml. of the zirconium-alizarin solution to the sample and to each comparison tube, mix well, and allow to stand about 18 hours. Comparison may be made in a 3-hole colorimeter. If the color of the sample does not match that of any of the comparison tubes, use a smaller volume of the sample.

Organic matter and phosphates interfere seriously, although small quantities of bicarbonate, calcium, chloride, magnesium, sulfate, sodium, manganese, silicate, boron, copper, iron, and sulfide may not interfere. On the other hand, each of these substances will interfere if present in too great a concentration.

By the above method 0.00-0.12 mg. of fluoride can be determined, although by dilution or by using a smaller volume of sample this range may be extended.

Methods, or modifications of previously reported methods, for determining fluorides in water have been developed by Alimarin,<sup>21</sup> Casares and Casares,<sup>31</sup> Thompson and Taylor,<sup>32</sup> Elvove,<sup>29</sup> Sanchis,<sup>30</sup> Charonnat and S. Roche,<sup>33</sup> Barr and Thorogood,<sup>34</sup> and Lamar and Seegmiller.<sup>28</sup>

Special determinations of fluoride in various materials have been reported as follows: food products,<sup>35</sup> aluminum salts,<sup>36</sup> air,<sup>37</sup> dicalcium phosphate,<sup>38</sup> fluoride complexes,<sup>39,70</sup> plants<sup>40</sup> and teeth.<sup>41</sup>

Alimarin's colorimetric method for fluorine, and others based on the bleaching of the zirconium-alizarin lake, have not proved entirely satisfactory, since the fluorine content is not proportional to the color fading; and results obtained with this method have not proved sufficiently consistent to permit the construction of a curve which shows any definite relationship between the two. While studying this method Winter<sup>42</sup> observed that when an extremely dilute solution of a soluble fluoride is added to a small quantity of zirconium-alizarin lake, the color fades very slowly until the zirconium is completely transformed to the fluoride complex, and then the color is discharged quite suddenly. Using this sharp color change which occurs at the end-point of the  $\text{ZrF}_6^{-2}$  transformation, Willard and Winter<sup>43</sup> have proposed a precipitation method for the determination of fluoride with thorium nitrate as the precipitant and the zirconium-alizarin lake as the indicator. The pink color at the end-point is due to the formation of a thorium lake. The precipitation is based on the methods of Daladrier,<sup>45</sup> Pisani,<sup>46</sup> and Gooch and Kobayashi,<sup>44</sup> who determined fluoride by gravimetric precipitation as thorium fluoride, but in these earlier methods the precipitate was ignited to the oxide under suitable conditions, and the fluoride originally present calculated from the quantity of the oxide.

The precipitation titration of fluoride with thorium nitrate has proved to be one of the most important developments in fluorine analysis in many years, since excellent results are obtained by this method where the colorimetric determination has been less satisfactory. Another important advantage of the Willard-Winter method lies in the success with which fluoride may be removed from the presence of interfering substances. Ions such as calcium, barium, ferric, aluminum, phosphate, arsenate, and sulfate, which precipitate or form complexes with zirconium or fluoride, interfere seriously and must be absent during the deter-

mination. This separation consists of volatilizing the fluoride as hydrofluosilicic acid by adding sulfuric or perchloric acid, water, and several pieces of glass to the sample in a distilling flask and distilling. The serious effect of any sulfuric acid which may be carried over during the distillation argues rather strongly for the use of perchloric acid. Another advantage of the latter lies in the fact that most perchlorates are soluble. The hydrofluosilicic acid may be used directly for the fluoride determination. This distillation separation has been studied critically by Winter and Butler,<sup>47</sup> Shuey,<sup>48</sup> and by Reynolds.<sup>49</sup>

The following titration procedure may be used in the absence of interfering substances:

**Indicator.** *Solution a:* Dissolve 1 g. of  $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$  in 250 ml. of water.

*Solution b:* Dissolve 1 g. of sodium alizarinsulfonate in 100 ml. of alcohol. Filter off any residue, and add 150 ml. of alcohol to the filtrate.

To use, mix 3 parts of solution *a* with 2 parts of solution *b*.

**Procedure.** Dissolve the weighed fluoride in water and dilute to a given volume. Transfer an aliquot portion to a tall beaker, add water to make the volume approximately 20 ml., and add 3 drops of indicator. If necessary add just enough dilute hydrochloric acid to destroy the color. Add an equal volume of neutral ethyl alcohol and titrate over a white surface in good light with standard thorium nitrate solution to the faint reappearance of color. The reaction is slow near the end-point. The concentration of the thorium nitrate is usually 0.01 N or 0.001 N, depending on the concentration of the fluoride in the unknown, and the volume of the solution used. With 0.01 N thorium nitrate a correction must be made for the amount of fluorine which combines with the indicator.

By keeping the volume of the solution to 10 ml., duplicate titrations agree within 0.1 ml. of 0.01 N thorium nitrate, which is equal to 0.02 mg. of fluoride. From 0.2-2.0 mg. of fluoride may be determined by this procedure.

Hoskins and Ferris<sup>60</sup> report that the analysis of a sample containing 57-760% of fluorine gives results which are 99 per cent accurate when 50-ml. portions of the solution are used; and that the same accuracy is possible with samples containing 6-90% by using 5 ml. of solution. Chlorides interfere somewhat, but by adding an equal quantity of chloride to a blank this interference is rendered negligible.

Armstrong<sup>61</sup> suggests that a 0.05 per cent aqueous solution of sodium alizarinsulfonate is superior to the zirconium-alizarin lake as an indicator, since with its aid a sharper end-point is obtained. This author<sup>62</sup> suggests that it is best to reduce the volume of the solution to 2 ml., and to use a 0.0004 N solution of thorium nitrate instead of the more concentrated solutions commonly used. The accuracy of the method using solutions containing 2-25% of fluoride is good. Frers and Lauckner<sup>58</sup> have used a modification of the Willard and Winter method, employing a zirconium lake formed with alizarinsulfonic acid and quin-alizarin as indicator.

In a recent study, Rowley and Churchill<sup>64</sup> titrated fluoride with a 0.1 N thorium nitrate solution in an aqueous solution instead of in 48 per cent ethyl

alcohol (as recommended by Willard and Winter) by closely controlling the pH of the solution titrated. A pH of 2.9-3.1 is suitable, and this may readily be attained by using monochloroacetic acid one-half neutralized with sodium hydroxide. The end-point appears more sharply under these conditions. In the alcohol solution, approximately 20 mg. or less of fluoride can be titrated satisfactorily, but with greater amounts the end-point is indefinite. In an aqueous medium 50 mg. of fluoride can be titrated to a definite end-point.

Markova<sup>55</sup> has used the method of Willard and Winter to determine fluoride in minerals, and Winter<sup>42</sup> has applied the procedure to the determination of fluoride in plants.

A titration method using alizarinsulfonic acid as an indicator and zirconium nitrate as the titrant has been used by Ugnyachev and Bilenko,<sup>56</sup> but apparently this procedure does not compare too favorably with other methods, since it is little used. The end-point of this titration is reached when the color of the solution turns from greenish-yellow to pink.

Recently Nolke<sup>71</sup> suggested a titration method for determining fluoride based upon the decolorization of the red-violet zirconium-alizarin lake by titration with a solution of the fluoride in acetic acid. The fluoride-acetic acid solution is added from a buret, and the end-point is indicated by the yellow color of free alizarinsulfonic acid. This color is made more perceptible by the addition of a little amyl alcohol in which the alizarinsulfonic acid dissolves.

**Detection of zirconium and hafnium.** Alizarinsulfonic acid gives a violet coloration with zirconium, and also with aluminum, yttrium, cerium, erbium, thallium, columbium, tungsten, titanium, thorium, molybdenum, and uranium. The coloration produced by zirconium, however, is stable in acid solutions, while the color reactions with all of the other metals disappear on the addition of concentrated hydrochloric acid.<sup>18,78</sup> Hafnium resembles zirconium in its reaction with alizarinsulfonic acid. In concentrated hydrochloric acid solutions, the color of the hafnium-alizarin lake fades sooner than that of the zirconium-alizarin lake, but not so soon as the thorium lake.<sup>19</sup>

Charonnat<sup>23</sup> has shown that the character of the zirconium-alizarin reaction is influenced by the relative quantities of zirconium and alizarinsulfonic acid used. This is shown in Table 57.

TABLE 57.—REACTION OF ZIRCONIUM AND ALIZARINSULFONIC ACID

Atoms of Zr	Moles of alizarin S	Character of reaction
1	2	Orange-yellow solution
2	1	Complete precipitation
4	1	Red-violet solution

The differences in the reactions are attributed to the formation of a dizirconyl-alizarin complex in combination with alizarinsulfonic acid (yellow solution) or with  $\text{ZrO}(\text{NO}_3)_2$  (red-violet solution). The solutions are stable in neutral or alkaline solutions, but the addition of acid causes the flocculation of the dye,

which redissolves when more acid is added. Fluorides seriously interfere with the zirconium reaction by forming a complex ion.

**Detection of boron.** A number of hydroxyanthraquinone dyes dissolve in concentrated sulfuric acid with the formation of intensely colored solutions, and these solutions undergo characteristic color changes in the presence of boric acid. These color changes appear to be caused by the formation of inner-complex boric acid esters or boric-sulfuric esters (page 407).

Alizarinsulfonic acid, purpurin, and quinalizarin are best suited for the detection of boron by methods based on this reaction, but alizarinsulfonic acid appears to be the least sensitive of the three.<sup>57</sup>

**Procedure.** Evaporate a drop of solution to be tested to dryness in a porcelain dish, and treat the residue with 2-3 drops of a 0.2 per cent solution of alizarinsulfonic acid in concentrated sulfuric acid and warm gently. The evaporation of the test solution should take place in the presence of alkalis to avoid the loss of boric acid with steam. A yellowish-red to red color appears if only 1.0 $\gamma$  of boron is present.

Fluorides and such oxidizing agents as nitrates and ferricyanides interfere, although the latter may be removed by ignition of the dried residue. When the above test is viewed under filtered ultra-violet light, as little as 0.02 $\gamma$  of boron may be detected.<sup>58</sup> Most common ions do not interfere. If iodide is present it may be removed by the addition of powdered silver sulfate. Interference by chlorate is avoided by using formaldehyde, and antimony is rendered harmless by the use of chlorine water. Less interference is encountered in making this test under ultra-violet light, and this is particularly true when silicate, bromide, nitrate, cobalt, and chromium are present.

**Determination of boron.** Dickinson<sup>69</sup> has proposed a method for the colorimetric determination of boron in plant material based upon the color reaction between boric acid and alizarinsulfonic acid. The color obtained is matched with that of a series of standards prepared from methyl orange.

**Procedure.** Ash 0.5-1.0 g. of the material in a porcelain crucible at 480-525° C., and to the ash add exactly 5 ml. of 0.4 N sulfuric acid. Triturate with a rubber-tipped stirring rod. Allow the residue to settle, and pipet off 1 ml. of the clear supernatant liquid into a special test tube. Add 9 ml. of a solution containing 0.01 g. of alizarinsulfonic acid. Mix, cool if necessary, let stand for 30 minutes, and match the color with that of methyl orange standards.

To prepare the methyl orange standards, dissolve 0.1 g. of the compound in 100 ml. of 95 per cent alcohol and 100 ml. of water, and standardize as follows: Prepare a series of boric acid solutions, containing up to 0.005 mg. of boron per ml., and mix 1 ml. of each with 9 ml. of the alizarinsulfonic acid solution used in the determination. Allow to stand for 30 minutes for the color to develop, and then run the methyl orange solution from a buret into a precisely similar tube until the colors match on looking down into the tubes. The results

obtained using this method agree within 0.2% of the quantity actually present.

**Detection of scandium.** With sodium alizarinsulfonate, and in the presence of dilute acetic acid, scandium gives a violet precipitate.<sup>59</sup> With this reaction 0.1 mg. of scandium can be detected. Other rare earths give no precipitate unless the solution is very concentrated. Scandium and thorium may be separated from the remaining rare earths by this reaction, even though only small quantities of scandium are present.<sup>60</sup>

**Detection of lithium.** Germuth and Mitchell<sup>62</sup> have used a 0.5 per cent solution of alizarinsulfonic acid as a reagent for lithium with which it yields a yellow coloration. In a recent review of various lithium tests, Karaoglanov<sup>61</sup> reports that alizarinsulfonic acid is more sensitive than sodium carbonate, ammonium carbonate, disodium phosphate, and disodium arsenate, and under favorable conditions 0.6 g. LiCl in 10 ml. of solution may be detected by using 1 ml. of 0.125 per cent of alizarinsulfonic acid solution. This is a more sensitive reaction than that of Germuth and Mitchell, which employs a more concentrated reagent. For the following reasons, however, alizarinsulfonic acid is not entirely satisfactory as a lithium reagent: <sup>61,68</sup>

- (1) The color tone does not depend entirely upon the presence of lithium.
- (2) Many substances cause color changes with alizarinsulfonic acid.
- (3) The color change with lithium chloride does not always appear to be reproducible.
- (4) The reaction requires extreme care in development.

**Detection of calcium, barium, and strontium.** When alizarinsulfonic acid is added to a solution containing calcium, barium, or strontium ions, and then the mixture made alkaline with sodium carbonate, a purple precipitate is formed. This may serve as a test for the alkaline earth metals, but it appears to have no great value, due largely to the fact that so many ions interfere.<sup>63</sup>

**Detection of beryllium.** Beryllium may be detected in the analysis of the aluminum group by means of the bluish-purple color formed when a 1 per cent solution of alizarinsulfonic acid is added to an alkaline solution of beryllium.<sup>65</sup>

**Detection of potassium.** Alizarinsulfonic acid has been proposed as a reagent for the microscopic detection of potassium, but Frediani and Gamble<sup>64</sup> find that this method is unsatisfactory. It seems that this reagent has been reported by mistake.

**Reactions with various cations.** Alizarinsulfonic acid gives color reactions with many ions not individually discussed in the above sections. A summary of many reactions of the dye with various ions is contained in Table 58, which is taken from the work of Germuth and Mitchell.<sup>66</sup>

Alizarinsulfonic acid is particularly sensitive toward uranium, platinum, stannic, titanous, aluminum, bismuth, ferric, chromic, cupric, mercuric, and thallium salts.



**Detection of thallium.** A 0.5 per cent solution of alizarinsulfonic acid reacts with solutions of thallium salts to give a dark blue solution or a bluish precipitate.<sup>66,76</sup>

**Detection of lead.** Lead may be detected by the purplish-red precipitate which forms when a 0.5 per cent solution of alizarinsulfonic acid is added to a solution of a lead salt.<sup>66,77</sup>

**Detection of thorium.** Wenger and Duckert<sup>72</sup> have studied the use of alizarinsulfonic acid as a reagent for thorium<sup>68,75</sup> and report that the reaction is not sensitive and is too general.

TABLE 58.—REACTIONS OF ALIZARINSULFONIC ACID WITH THE METALS

(Use 5 ~~ml.~~ portions of 1 per cent test solution with 0.3 ml. of 0.5 per cent alizarinsulfonic acid)

Compound	Color of ppt.	Coloration
Pb(NO <sub>3</sub> ) <sub>2</sub>	Purplish-red	.....
AgNO <sub>3</sub>	.....	Dark brown
Hg(NO <sub>3</sub> ) <sub>2</sub>	Dark red	.....
HgNO <sub>3</sub>	.....	Light yellow
Bi(NO <sub>3</sub> ) <sub>3</sub>	Pink-red	.....
CuCl <sub>2</sub>	Light red	.....
CdCl <sub>2</sub>	Orange	.....
SbCl <sub>5</sub>	Light red	.....
SbCl <sub>3</sub>	.....	Deep red
SnCl <sub>4</sub>	Orange	.....
SnCl <sub>2</sub>	Pink	.....
MnCl <sub>2</sub>	.....	Yellow
FeCl <sub>3</sub>	Smoky black	.....
FeCl <sub>2</sub>	Dark red	.....
CoCl <sub>2</sub>	Red	.....
NiCl <sub>2</sub>	.....	Red
CaCl <sub>2</sub>	.....	Red
Ba(NO <sub>3</sub> ) <sub>2</sub>	.....	Light red
Sr(NO <sub>3</sub> ) <sub>2</sub>	.....	Deep red
ZnCl <sub>2</sub>	.....	Pink
MgCl <sub>2</sub>	Light red	.....
NaCl	.....	Yellow
KCl	.....	Yellow
NH <sub>4</sub> Cl	Dark yellow	.....
LiCl	.....	Yellow
AlCl <sub>3</sub>	Tawny red	.....
CrCl <sub>3</sub>	Deep yellow	.....
UO <sub>2</sub> Cl <sub>2</sub>	Deep violet	.....
H <sub>2</sub> PtCl <sub>6</sub>	Purple	.....
PtCl <sub>2</sub>	Deep red	.....
AuCl <sub>3</sub>	.....	Light red
AuCl	.....	Dark red
Th(NO <sub>3</sub> ) <sub>4</sub>	.....	Red
TiNO <sub>3</sub>	Dark blue	.....
TiCl <sub>3</sub>	Black	.....

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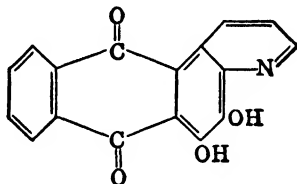
## ALIZARIN BLUE S

Beil. Ref. XXI, 632, 633.

**Use:** Detection of hafnium and zirconium.

Alizarin blue S may be used as a reagent for zirconium and hafnium.<sup>1</sup> It resembles purpurin, alizarinsulfonic acid, and rufigallic acid in its reactions with these metals, giving characteristic colors with aqueous solutions of their salts.

Alizarin blue S is prepared by the action of sodium bisulfite on alizarin blue,<sup>2</sup> which has the following composition



Alizarin blue S corresponds to the product formed by the addition of two molecules of sodium bisulfite to 1 molecule of alizarin blue,  $[C_{17}H_9O_4N + 2NaHSO_3]$ .

It occurs as red-brown, microscopic crystals. It is very easily soluble in water, but only slightly soluble in alcohol.

1. J. H. de Boer, *Rec. trav. chim.* 44, 1071-6 (1925) ; *C.A.* 1042 (1926).
2. H. Brunck and C. Graebe, *Ber.* 15, 1783 (1882).

### 1,2,4,5,8-ALIZARIN CYANIN

Synonym: Alizarin cyanin R, Alizarin pentacyanin, 1,2,4,5,8-pentahydroxyanthraquinone

$C_{14}H_8O_7$

Mol. Wt. 288.20

Color Index, 1050.



**Use:** Detection of fluoride.

The dye crystallizes from nitrobenzene in brown leaflets. It is insoluble in water, but dissolves in acetic acid to form a yellowish-red solution which shows a green fluorescence. It also dissolves in sodium hydroxide with a blue solution, and in sulfuric acid with a blue solution which has a red fluorescence.

**Preparation:** Stir 5 g. of powdered, dry quinalizarin into 100 g. of concentrated sulfuric acid, and add 5 g. of finely powdered manganese dioxide so that the temperature at no time exceeds 25° C. Pour into water, avoiding too great a rise in temperature, and then add sodium bisulfite until the odor of sulfur dioxide persists after some time. The reduction of the quinone is indicated by a change in color from violet to reddish-brown. Boil the mixture, filter, and dissolve the residue in hot dilute sodium hydroxide. Filter and precipitate the dye from the filtrate with hydrochloric acid.

**Detection of fluoride.** 1,2,4,5,8-Alizarin cyanin, like alizarinsulfonic acid, purpurin, anthrapurpurin, flavopurpurin, and anthragallol, reacts with zirconium to form a color lake; and the color of this lake is discharged by reaction with fluoride ions. Shvedov<sup>1</sup> claims that 1,2,4,5,8-alizarin cyanin is the most sensitive fluoride indicator of the group of hydroxyanthraquinone dyes. It gives a maximum sensitivity of 0.01 mg. of fluoride per liter, and an average sensitivity of

0.02 mg. per liter. The reaction between fluoride and the alizarin cyanin lake takes place in 2-3 hours at room temperature, which greatly reduces the time of 18 hours required for the determination using alizarinsulfonic acid as proposed by de Boer. With 100 mg. of sample, the maximum sensitivity is obtained by the addition of 5 ml. of indicator and 10 ml. of 1/12 N hydrochloric acid. With an increase in the fluoride ion concentration, the color changes from the blue to the violet region of the spectrum. Potassium, sodium, calcium, magnesium, chloride, bromide, and nitrate do not influence the character of the reaction to any great extent; but, as with other hydroxyanthraquinone-fluoride indicators, aluminum, sulfate, phosphate, arsenite, and arsenate must be absent.

1. V. P. Shvedov, *Lab. Prakt. (U.S.S.R.)*, 2-3, 22-5 (1939) ; *C.A.* 33, 4546 (1939).

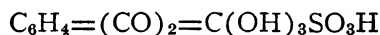
## ALIZARIN RED PS

Synonym : Purpurinsulfonic acid, 1,2,4-trihydroxy-3-anthraquinone-sulfonic acid

$C_{14}H_8O_8S$

Mol. Wt. 336.26

Beil. Ref. XI, 362.



**Use:** Detection of aluminum.

Alizarin red PS occurs as a red crystalline compound, which is only slightly soluble in cold water, but which is easily soluble in hot water with the formation of a yellowish-red solution. It dissolves in dilute alkalis with a red color.

**Preparation:** Sulfonate purpurin by heating 10 g. of the dye with 20 g. of fuming sulfuric acid (20 per cent  $SO_3$ ) at 100° C.

**Detection of aluminum.** The dye alizarin red PS has been used by Eegriwe<sup>1</sup> as a reagent for aluminum. The reaction is quite sensitive, giving a fluorescent as well as color effect.

The test for aluminum is made as follows:

**Reagent.** Dissolve 0.1 g. of alizarin red PS in 100 ml. of water. Filter if necessary.

**Procedure.** In the analysis of the chromium, aluminum, zinc group, precipitate any chromate with barium chloride in a dilute acetic acid solution, and separate aluminum from zinc by the precipitation of aluminum hydroxide with an excess of ammonium hydroxide. Dissolve the aluminum hydroxide in a little hydrochloric acid and to one drop of this solution add one drop of the dye solution and mix well. To the acid, orange-yellow solution, add ammonium hydroxide dropwise to a faint alkaline reaction, and heat for a few minutes. Cool, and acidify with dilute acetic acid. A yellow fluorescence and a rose color appear in the presence of aluminum.

This test is excellent, and is sensitive to 0.5 $\gamma$  of aluminum. The limiting concentration is 1:10,000,000. Cobalt, chromium, iron, and copper give a similar reaction.

1. E. Eegriwe, *Z. anal. Chem.* **76**, 438-43 (1929) ; *C.A.* **23**, 2901 (1929).

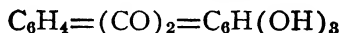
### ANTHRAGALLOL

Synonym: 1,2,3-Trihydroxyanthraquinone

$C_{14}H_8O_5$

Mol. Wt. 256.20

Beil. Ref. VIII, 505.



**Use:** Detection of tin.

Anthragallol occurs as fine bright-orange needles. It sublimes about 290° and melts at 313-314° with decomposition. The compound is only slightly soluble in water, chloroform, and carbon disulfide, but it is soluble in alcohol, ether, and acetic acid. It is soluble in concentrated sulfuric acid with a bright-red color, and it is precipitated unchanged on dilution. It is also soluble in alkalis forming green solutions, changing to brown in air; and is soluble in ammonium hydroxide yielding a dirty green solution, which becomes blue on standing or heating.

**Preparation:** Dissolve 36 g. of pure benzoic acid in 300 g. of sulfuric monohydrate with thorough stirring. Heat slowly to 90° C., and at this temperature add in small portions over a period of 1 hour 50 g. of pure gallic acid which has been dried at 110° C. Then increase the temperature to 118° C. and keep at this temperature for 6 hours. At the end of the heating period, pour the melt cautiously into 1 liter of boiling water with continuous stirring. Filter the boiling mixture through a hot filter, and wash well with hot water. The excess benzoic acid crystallizes from the mother liquor.<sup>1</sup>

The gallic acid may be prepared by hydrolyzing tannin with 40 per cent sodium hydroxide at 70° C. with the addition of a little sodium bisulfite. Precipitate the gallic acid with concentrated hydrochloric acid, and recrystallize from water.

To purify the commercial product, recrystallize from nitrobenzene, convert to the triacetyl derivative with acetic anhydride and a few drops of sulfuric acid, purify the product by recrystallization from acetic acid, and hydrolyze by warming with 30 parts of 5 per cent alcoholic hydrochloric acid, from which the compound separates in the pure state.<sup>2</sup>

**Detection of tin.** Anthragallol contains hydroxyl groups in the 1,2-positions, and reacts somewhat like the other hydroxyanthraquinone dyes of this type. It has been studied by Eegriwe<sup>3</sup> as a reagent for stannic tin with which it gives an impure though sensitive color reaction. To make the test, substitute the dye for anthrapurpurin in the reaction using that reagent (see below).

1. C. Seuberlich, *Ber.* **10**, 39 (1877).

2. O. Dimroth, *Ann.* **446**, 110-111 (1926).

3. E. Eegriwe, *Z. anal. Chem.* **120**, 81-4 (1940) ; *C.A.* **35**, 48 (1941).

**ANTHRAPURPURIN**

Synonym: 1,2,7-Trihydroxyanthraquinone, isopurpurin, oxyiso-anthraflavinic acid

 $C_{14}H_8O_6$ 

Mol. Wt. 256.20

Beil. Ref. VIII, 516.



**Use:** Detection of tin.

Anthrapurpurin crystallizes as orange-colored needles from alcohol. The compound melts at 369°, boils at 462° with partial decomposition, and sublimes at 170°. It is almost insoluble in boiling acetic acid and chloroform, but is easily soluble in boiling alcohol and in boiling barium hydroxide solution to which it imparts a violet color. It also dissolves in potassium hydroxide, ammonium hydroxide and sodium carbonate to yield violet solutions; in pure concentrated sulfuric acid with the formation of a red-brown color; and in nitric acid with a red-violet color.

**Preparation:** Mix 200 g. of sodium anthraquinone-2,7-disulfonate with 40 g. of potassium chlorate, 700 g. of sodium hydroxide and 1260 ml. of water, and heat at 170° C. under 5 atmospheres pressure. For the recovery of the reagent, treat the reaction mixture as described for the preparation of alizarin (page 410).<sup>1</sup>

**Detection of tin.** Anthrapurpurin reacts with stannic tin to give an orange-yellow color. This reaction may be used for the detection of tin.<sup>2</sup>

The test is carried out as follows:

**Reagent.** Dissolve 0.1 g. of anthrapurpurin in 100 ml. of methyl alcohol. Since anthrapurpurin does not dissolve to give a clear solution, use the clear yellow supernatant liquid obtained on standing.

**Procedure.** To 1 drop of solution to be tested, add 1 drop of anthrapurpurin solution (yellow color). Then add dropwise a solution obtained by dissolving 15 g. of pure ammonium carbonate in 200 ml. of water to the test solution until the reaction is basic (red solution). Next add dropwise a solution prepared by mixing 30 volumes of acetic acid with 60 volumes of water until the mixture is acid (use smallest possible drops). Orange to orange-red colors and precipitates are observed, depending on the concentration of the stannic ion. With 5γ of tin and 1 drop of anthrapurpurin solution, an orange precipitate forms on standing. With 0.2γ of tin in 1 drop of solution (0.04 ml.) and 1 drop of reagent, an orange-yellow color appears.

Under similar conditions titanium gives a red color, zirconium a violet color, and aluminum a carmine color. Molybdates give a brownish-yellow color and eventually a brown precipitate. Iron gives a brown tint, chromium a dirty red color, and bismuth a pink precipitate.

The presence of antimony interferes somewhat with the test, but 0.3γ of tin can be detected in the presence of 1.5 mg. of antimony.

1. W. H. Perkin, *J. Chem. Soc.* **37**, 557.
2. E. Eegriwe, *Z. anal. Chem.* **120**, 81-4 (1940); *C.A.* **35**, 48 (1941).

**ANTHRARUFIN**

Synonym: 1,5-Dihydroxyanthraquinone

 $C_{14}H_8O_4$ 

Mol. Wt. 240.20

Beil. Ref. VIII, 453.

**Use:** Detection of nitric acid.

The reagent melts at 280° C., and sublimes easily in pale yellow leaflets. It is almost insoluble in water, ammonium hydroxide, sodium carbonate, and barium hydroxide, but it is easily soluble in dilute potassium hydroxide with a violet-red color and in concentrated sulfuric acid with an intense red color and fluorescence. It is difficultly soluble in alcohol and acetic acid, and only slightly soluble in ether and benzene.

**Preparation:** Anthrarufin is formed as the principal product as the sulfuric ester when 50 parts of anthraquinone and 20 parts of boric acid stand 36 hours with 1000 parts of fuming sulfuric acid (80 per cent  $SO_3$ ) under pressure at 100° C. The ester is saponified by heating with dilute sodium hydroxide.

The reagent is also obtained with anthraflavinic acid and 1,7-dihydroxyanthraquinone when *m*-hydroxybenzoic acid is heated with sulfuric acid.<sup>1</sup>

**Detection of nitric acid.** A solution of anthrarufin in concentrated sulfuric acid is bright red in color, but when the sulfuric acid contains as little as 0.004 per cent by weight of nitric acid a yellow coloration appears. This test is more sensitive than the familiar "brown ring" test, which in the presence of halogens may prove unreliable.<sup>2,3</sup>

**Reagent.** As reagent use a solution prepared by dissolving 0.2126 g. of anthrarufin in 250 ml. of concentrated sulfuric acid (nitric acid-free).

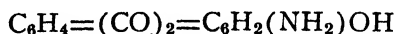
**Procedure.** Prepare a solution or suspension of the material to be tested in concentrated sulfuric acid so that at least 0.002 per cent nitric acid is present. To 10 ml. of this solution add one drop of the anthrarufin solution prepared above. Let stand one minute and observe the color. Compare with a similar quantity of sulfuric acid and one drop of the anthrarufin solution. A color change from red to yellow is a positive test.

1. E. Schunck and H. Roemer, *Ber.* **11**, 1176 (1878).
2. J. Wilson, *J. Soc. Chem. Ind.* **44**, 438T (1925); *C.A.* **19**, 3071 (1925).
3. G. Gutzeit, *Helv. Chim. Acta.* **12**, 713, 829 (1929).

**1-AMINO-4-HYDROXYANTHRAQUINONE** $C_{14}H_9O_3N$ 

Mol. Wt. 239.22

Beil. Ref. XIV, 268.

**Use:** Detection of beryllium, boron, lithium and thorium.



The compound is obtained as a red-violet crystalline powder from alcohol or water. It is soluble in alcohol and benzene with a fuchsin-red color. It also dissolves in sodium hydroxide solutions with a violet color, and in sulfuric acid with a yellow color. Alcoholic and acid solutions of the dye fluoresce red, while alkaline solutions do not fluoresce. The melting point is 207-8°.

**Preparation:** 1-Amino-4-hydroxyanthraquinone is prepared by condensing *p*-aminophenol with phthalic anhydride.

**Detection of beryllium and lithium.** 1-Amino-4-hydroxyanthraquinone reacts with beryllium and lithium in an alkaline solution and with thorium in an acid solution to give an intense fluorescence. These reactions may be used for the detection of beryllium, lithium and thorium.<sup>1</sup>

**Reagent.** Dissolve 0.1 g. of the dye in 100 ml. of 95 per cent ethyl alcohol.

**Procedure.** Place 0.1 ml. of the beryllium solution (containing about 0.1 g. Be per liter) in a test tube and add 1 ml. of 2.5 N sodium hydroxide. Dilute to 10 ml. and add 0.5 ml. of the reagent and examine under ultra-violet light.

Lithium gives a similar reaction with as little as 0.7 mg. in 1 ml. of solution. Calcium ions in saturated calcium hydroxide also produce a faint fluorescence and are likely to interfere. Oxidizing agents destroy the dye, although the latter seems stable in air.

**Detection of thorium.** To test for thorium, make the pH of the test solution about 2.0 and proceed as with beryllium. The sensitivity of the thorium reaction is not great.

**Detection of boron.** A solution of 1-amino-4-hydroxyanthraquinone in sulfuric acid gives an intense orange-brown fluorescence with small quantities of boron. As little as 1 drop of a solution containing 1 g. of borax in 10 liters gives the test.<sup>2</sup>

1. C. E. White and C. S. Lowe, *Ind. Eng. Chem., Anal. Ed.* **13**, 809-10 (1941); *C.A.* **36**, 55 (1942).
2. J. H. Radley, *Analyst.* **69**, 47-8 (1944); *C.A.* **38**, 1974 (1944).

## CARMINE RED

**Use:** Detection of boric acid.

Carminic acid is the product obtained by boiling a dilute aqueous solution of carminic acid with a few drops of hydrochloric acid. Since carminic acid is a glucosidal derivative of a rather complex hydroxyanthraquinone, it appears probable that carmine red, which is formed by hydrolysis, is an hydroxyanthraquinone having hydroxyl groups in the 1,2-positions at least. For this reason carmine red reacts somewhat like alizarin and similar compounds, giving color reactions with boron and forming lakes with various metals.

**Detection of boric acid.** The only analytical use reported for this dye is the detection of boric acid. Zorkin<sup>1</sup> has found that a 0.05 per cent solution of carmine red in concentrated sulfuric acid changes from red to blue in the presence of boric acid. As little as 0.1γ of boron in 0.03 ml. of solution gives this reaction. The test may be made on natural salt solutions and minerals.

Dobbins and Kapp<sup>2</sup> have used this reaction for the detection of borates in a scheme for the analysis of the anions.

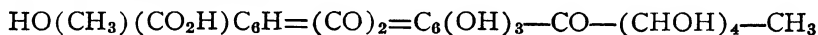
1. F. P. Zorkin, *J. Applied Chem. (U.S.S.R.)*, **9**, 1505-6 (1936); *C.A.* **31**, 2124 (1937).
2. J. T. Dobbins and M. E. Kapp, *J. Chem. Ed.* **20**, 118-20 (1943).

## CARMINIC ACID

$C_{22}H_{20}O_{13}$

Mol. Wt. 492.38

Carminic acid is a rather complex hydroxyanthraquinone derivative obtained from cochineal (*Coccus cacti* L.). It is a glucosidal coloring matter corresponding to the following formula

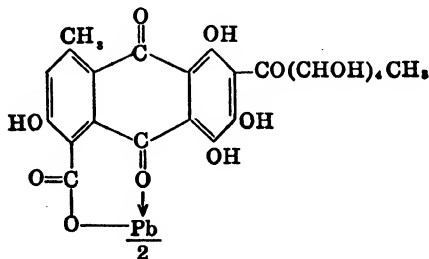


**Use:** Detection of aluminum, cerium, lead and zirconium.

The molecule contains the same reactive groups as other of the hydroxyanthraquinone dyes, but in addition the carboxyl group may function as a part of the reactive structure giving rise to somewhat different derivatives.

Carminic acid is a dark, reddish-brown or bright red powder. It is soluble in water, alcohol, concentrated sulfuric acid, sodium hydroxide, and potassium hydroxide; but is insoluble in benzene and chloroform; and is only slightly soluble in ether. It decomposes at 135°. Its aqueous solution at pH 4.8 is yellow and at 6.2 violet.

**Detection of lead.** Pavelka has used carminic acid as a reagent for lead.<sup>1,5-7</sup> The lead complex probably has the following structure:



A spot test which will detect 0.001 mg. of lead is performed as follows:

**Reagent.** Impregnate a piece of filter paper with a 0.5 per cent ammoniacal solution of carminic acid and dry.

**Procedure.** Place a drop of the nearly neutral solution to be tested on the carminic acid test paper prepared above, expose to ammonia fumes, and then dry. A violet spot appears if lead is present. This reaction is sensitive to 1-6 $\gamma$  of lead.

An excess of copper prevents this reaction, but silver, bismuth, and cadmium do not interfere if the test solution is previously treated with ammonium hydroxide and ammonium acetate and then filtered. By this procedure bismuth hydroxide is precipitated; and the ammonia complexes of silver and cadmium, which are in the filtrate, do not interfere. This test is excellent.

Pavelka and Setta<sup>7</sup> have used carminic acid for the microchemical detection of lead as an impurity in ammonium molybdate.

**Detection of zirconium.** An acid solution of carminic acid is yellow in color, but in the presence of zirconium a coloration resembling that of the permanganate ion is obtained.<sup>2</sup>

**Reagent.** Dissolve carminic acid in sufficient 30 per cent alcohol to give a wine-red solution.

**Procedure.** Make solution to be tested 0.4 N in hydrochloric acid, add a little of the reagent, and then heat on a water bath. A violet-red color is a positive test.

To detect traces of zirconium, use only enough carminic acid to give a slight yellow tint to an acid solution. The sensitiveness is 1:100,000.

Titanium, sulfate, phosphate, and fluoride interfere and must be absent.

**Detection of cerium.** Herzfeld<sup>8</sup> has found carminic acid to be a useful reagent for cerium. The test has about the same sensitiveness as that with tannin, which detects 8 $\gamma$  of cerium.

**Reagent.** As reagent use a solution prepared by a ten-fold dilution of a saturated alcoholic solution of carminic acid with water.

**Procedure.** To solution to be tested, add 3 drops of a saturated solution of sodium acetate in 50 per cent glycerol, mix, and add 2 drops of the reagent. On standing, the reddish solution changes to blue-violet, and eventually becomes colorless under a quartz lamp.

**Detection of aluminum.** Carminic acid or tincture of cochineal produces colored precipitates with aluminum salts in neutral or weakly acid solutions.<sup>4</sup>

1. F. Pavelka, *Mikrochemie*, **7**, 301-4 (1929); *C.A.* **24**, 3965 (1930).
2. F. Pavelka, *Mikrochemie*, **8**, 345-51 (1930); *C.A.* **25**, 892 (1931).
3. E. Herzfeld, *Z. anal. Chem.* **115**, 421-3 (1939); *C.A.* **33**, 3289 (1939).
4. Luckow, *J. prakt. Chem.* **399** (1864).
5. J. V. Dubsky and J. Trtilek, *Chem. Obzor.* **9**, 68-9 (1934); *C.A.* **28**, 5001 (1934).
6. J. V. Dubsky, *Chem. Listy*, **34**, 91-3 (1940); *C.A.* **37**, 1947 (1943).
7. F. Pavelka and G. Setta, *Mikrochem. ver. Mikrochim. Acta*, **31**, 73-82 (1943); *C.A.* **38**, 1974 (1944).

## COCHINEAL

**Use:** Detection of aluminum, boron, copper, gold, lead, molybdenum, platinum, rare earths, thallium, tungsten, uranium, zinc and zirconium.

Neither cochineal, nor the tincture which is prepared from it, is a pure compound; but since both contain carminic acid (a hydroxyanthraquinone derivative) they resemble the hydroxyanthraquinone dyes in many of their analytical properties. Cochineal is the dried female insect, *Coccus cacti* L., enclosing the young larvae. It contains about 10 per cent carminic acid, about 2 per cent of wax (coccerin), and about 10 per cent of fat. The coloring matter is an alkali carminate, which is contained only in the fatty parts of the insect and in the yolk of the egg to the extent of about 10-14 per cent. Tincture of cochineal, which is the commonly used analytical reagent, may be prepared by extracting one part of cochineal with 80-100 parts of 25 per cent alcohol. Ammoniacal cochineal is apparently a derivative of carminic acid, in which an hydroxyl group has been replaced by an amino group.

As an analytical reagent, cochineal has proved particularly useful for the microchemical detection of the rare earths and zirconium, and for the fluorescent detection of thallium, copper, lead, platinum, gold, molybdenum, aluminum, zinc, tungsten, and boron. Uranium salts also give color reactions with cochineal.

**Detection of lead.** Pavelka<sup>18,15-17</sup> has used carminic acid, which is obtained from cochineal, for the detection of lead. For the details of this test, see section on carminic acid (page 443).

**Detection of the rare earths.** The rare earths and zirconium compounds give violet colored solutions with tincture of cochineal, while thorium salts give blue solutions.<sup>1</sup> This reaction, however, is not recommended by Wenger and Duckert,<sup>12</sup> who have reviewed the various methods which have been proposed for the detection of thorium. Not only is cochineal useful for the detection of the rare earths as a group, but in conjunction with acetic acid it may be used to differentiate between the cerite earths from lanthanum to samarium on the one hand and terbium and erbium on the other. The red-violet color caused by the addition of tincture of cochineal to solutions of lanthanum salts is changed to an orange-red (the original color of cochineal) upon the addition of 2 per cent acetic acid. Solutions containing praseodymium and cerium behave similarly. A more concentrated acetic acid is necessary to restore the cochineal color in solutions containing neodymium and samarium. A 30 per cent solution of acetic acid changes the color of terbium and erbium solutions only to red. From the violet solutions of the rare earths from europium to ytterbium, red-violet flocks gradually separate, while the orange-yellow solutions of the cerite earths from lanthanum to samarium remain clear.

Lead and copper interfere with these reactions. Beryllium, aluminum, and gallium salts give a rose color with intensive red fluorescence in ultra-violet light. Zinc, mercury, cadmium, calcium, magnesium, strontium, barium, nickel, cobalt, and manganese give red precipitates; and uranyl, ferric, and chromic ions give

dark colored precipitates. It appears, therefore, that the red-violet color given by the rare earths need not be confused with color reactions of the other metals.<sup>1</sup> About 10 $\gamma$  of the rare earths in one ml. can be detected.

**Detection of scandium.** Scandium solutions also become violet when mixed with tincture of cochineal, and this color does not disappear on the addition of concentrated acetic acid. If the violet scandium solution is made alkaline with ammonium hydroxide, a blue-violet precipitate appears, and on addition of ammonium carbonate this precipitate dissolves with the formation of a violet color. When this solution is acidified with concentrated acetic acid it becomes blue, and this color does not disappear with the addition of hydrochloric acid. After 6-12 hours a blue violet precipitate forms. Zirconium, thorium, and the remaining rare earths do not show this behavior.

**Detection of uranium.** A cochineal solution containing alum is colored green by uranium salts.<sup>3</sup> Upon the addition of an aqueous solution of uranyl nitrate to a neutral amyl alcohol solution of ammoniacal cochineal, the aqueous layer becomes an amethyst color.<sup>4</sup>

**Fluorescence analysis.** Tincture of cochineal causes a marked fluorescence with many ions, and may be used as a special analytical reagent for many substances.<sup>2,5-9</sup> The fluorescence is usually caused by excitation with ultra-violet light. This reaction may be used for the following substances:

(a) *Molybdic acid:* Tincture of cochineal gives a fire-red fluorescence with solutions of molybdic acid. Silver, cadmium, arsenic, antimony, zinc, calcium, strontium, barium, potassium, sodium, ammonium and tungsten do not interfere, but lead, mercury, copper, bismuth, cobalt, nickel, iron, manganese, chromium and vanadium must be absent. The molybdenum test is carried out at pH 4.8-6.2.<sup>2,10</sup>

(b) *Boric acid:* With tincture of cochineal, boric acid yields a bright orange-yellow fluorescence. Silver, mercury, arsenic, antimony, calcium, strontium, barium, potassium, sodium and ammonium ions do not interfere, but lead, copper, cadmium, cobalt, nickel, iron, zinc, manganese and chromium should be absent. Aluminum and magnesium also cause a fluorescence, but the color is not similar to that produced by boric acid.<sup>7,11,14</sup>

(c) *Thallium:* The fluorescence of an alkaline cochineal solution is destroyed by as little as 0.5 $\gamma$  of trivalent thallium.<sup>5</sup>

(d) *Copper:* As little as 0.1 $\gamma$  of copper changes the fluorescence of cochineal from red to a faint bluish-white. Gold, platinum and lead interfere.<sup>5</sup>

(e) *Platinum:* The violet-red fluorescence of cochineal is destroyed by as little as 2.5 $\gamma$  of platinum.<sup>5</sup>

(f) *Gold:* Gold gives a pale green fluorescence with cochineal in the presence of alkali hydroxides.<sup>5</sup>

(g) *Aluminum:* Cochineal gives a red fluorescence with only 0.1 $\gamma$  of aluminum.<sup>5</sup>

(h) *Zinc*: Zinc shows the same characteristics as aluminum.<sup>5</sup>

(i) *Cobalt*: Cochineal causes a fluorescence with 0.5γ of cobalt. Nickel, manganese and iron interfere.<sup>9</sup>

(g) *Beryllium*: Cochineal causes a fluorescence with only 0.05γ of beryllium. This may be differentiated from the fluorescence caused by aluminum.<sup>9</sup>

(k) *Thorium*: The fluorescence of cochineal is destroyed by 1γ of thorium in alkaline solutions. This is probably caused by the adsorption of the dye by thorium hydroxide.<sup>9</sup>

(l) *Tungsten*: Tungsten causes a fluorescence similar to that with aluminum.<sup>9</sup>

The intensity of the red fluorescence produced by excitation of solutions of cochineal and tungsten, molybdenum, and aluminum with ultra-violet light may be used for the colorimetric estimation of these metals.<sup>6</sup>

1. G. Beck, *Mikrochemie*. **27**, 47-51 (1939); *C.A.* **33**, 5772 (1939).
2. L. Szebelledy and J. Jonas, *Magyar Gyogyyszeresztud. Tarsasag Ertesitoje*. **12**, 412-16 (1936); *C.A.* **31**, 1323 (1937).
3. Crolas and Ducker, *Arch. Pharm.* **2**, 246.
4. C. F. Muttelet, *Ann. fals.* **10**, 228-30 (1917); *C.A.* **12**, 460 (1918).
5. H. Gotō, *Science Repts. Tōhoku Imp. Univ. First Ser.* **29**, 204-18 (1940); *C.A.* **35**, 1720-3 (1941).
6. H. Gotō, *J. Chem. Soc. Japan*. **60**, 937-9 (1939); *C.A.* **34**, 4355 (1940).
7. L. Szebelledy and J. Gaal, *Magyar Gyogyyszeresztud. Tarsasag Ertesitoje*. **10**, 309-13 (1934); *C.A.* **28**, 5365 (1934).
8. H. Gotō, *J. Chem. Soc. Japan*. **59**, 547-54 (1938); *C.A.* **32**, 5721 (1938).
9. H. Gotō, *Science Repts. Tōhoku Imp. Univ. First Ser.* **29**, 287-303 (1940); *C.A.* **35**, 1720-3 (1941).
10. L. Szebelledy and J. Jonas, *Mikrochim. Acta*. **1**, 46-50 (1937); *C.A.* **31**, 5718 (1937).
11. M. Haitinger, *Microchemie*. **16**, 321-56 (1934); *C.A.* **29**, 2470 (1935).
12. P. Wenger and R. Duckert, *Helv. Chim. Acta*. **25**, 1110-14 (1942); *C.A.* **37**, 575 (1943).
13. J. V. Dubsky and J. Trtílek, *Chem. Obzor*. **9**, 68-9 (1934); *C.A.* **28**, 5001 (1934).
14. L. Szebelledy and J. Gaal, *Z. anal. Chem.* **98**, 255 (1934).
15. F. Pavelka, *Mikrochemie*. **7**, 301-4 (1929); *C.A.* **24**, 3965 (1930).
16. G. Sensi and S. Seghezzo, *Ann. chim. appl.* **19**, 392 (1929).
17. G. Sensi and S. Seghezzo, *Mikrochemie*. **8**, 210 (1930).

## 1,8-DIHYDROXYANTHRAQUINONE

Synonym: Chrysazin

$C_{14}H_8O_4$

Mol. Wt. 240.20

Beil. Ref. VIII, 458.

Color Index, 1030.



**Use:** Detection of beryllium.

This compound is obtained as red needles with a bluish luster when crystallized from alcohol. The melting point is 191° C. It is insoluble in water, but is moderately soluble in alcohol, ether, acetic acid, and chloroform. It dissolves in sodium hydroxide to form a red solution. The sulfuric acid solution is also red.

**Preparation:** 1,5- and 1,8-anthraquinone disulfonic acids are prepared as the first step in this synthesis. Mix intimately 100 g. of anthraquinone with

1 g. of precipitated mercuric oxide and 200 g. of fuming sulfuric acid (40-45 per cent  $\text{SO}_3$ ). Heat to  $130^\circ\text{C}$ . after which the reaction proceeds strongly. The temperature should not rise above  $150^\circ\text{C}$ . Continue the heating until a drop of the reaction mixture when poured into water remains perfectly clear, and until the anhydride is completely or almost gone. At this point the 1,5-disulfonic acid is quantitatively precipitated, while the 1,8-disulfonic acid remains in solution. Filter, and mix the filtrate with an equal volume of water. The 1,8-anthraquinonedisulfonic acid separates as needles, and these may be recrystallized from hydrochloric acid.

Heat the 1,8-anthraquinonedisulfonic acid with 1-2 parts of calcium hydroxide and 10-20 parts of water at  $180\text{--}200^\circ\text{C}$ . for 4 hours to convert the compound to the dihydroxyanthraquinone.<sup>2,3</sup>

**Detection of beryllium.** 1,8-Dihydroxyanthraquinone reacts with beryllium in an alkaline solution to give a red fluorescence. This fluorescence is somewhat less intense than that with 1-amino-4-hydroxyanthraquinone, but it may be used to detect beryllium in solutions as dilute as 1:1,000,000. The smallest quantity of beryllium detectable by this method is 0.01 mg. Neither beryllium or thorium fluoresce in acid solutions of the reagent. Other ions soluble in sodium hydroxide interfere.<sup>1</sup>

1. C. E. White and C. S. Lowe, *J. Ind. Eng. Chem., Anal. Ed.* **13**, 809-10 (1941).
2. R. E. Schmidt, *Ber.* **37**, 68 (1904).
3. C. Liebermann, *Ann.* **183**, 184 (1876); *Ber.* **11**, 1610 (1878).

## FLAVOPURPURIN

Synonym: 1,2,6-Trihydroxyanthraquinone

$\text{C}_{14}\text{H}_8\text{O}_5$

Mol. Wt. 256.20

Beil. Ref. VIII, 513.



**Use:** Detection of tin.

Flavopurpurin is obtained as golden yellow needles from alcohol. The melting point is above  $330^\circ\text{C}$ . The compound boils at  $459^\circ\text{C}$ . with partial decomposition. It sublimes at  $160^\circ\text{C}$ . as red-yellow needles. It is moderately soluble in boiling water, difficultly soluble in ether, and easily soluble in alcohol and benzene. It is soluble with a purple color in potassium hydroxide, with a yellow-red color in ammonium hydroxide and sodium carbonate, and with a red-violet color in hot barium hydroxide. It also dissolves in pure concentrated sulfuric acid with a red-violet color.

**Preparation:** Flavopurpurin is prepared by heating 8 g. of 1,6-dihydroxyanthraquinone with 8 g. potassium nitrate and 1 liter of sodium hydroxide ( $45^\circ\text{Bé}$ ) under pressure for 12 hours to  $175^\circ\text{C}$ . For the preparation of 1,6-dihydroxyanthraquinone, see method of Frobenius and Hepp.<sup>1</sup>

**Detection of tin.** Flavopurpurin has not been used to any great extent as an analytical reagent, but since it contains hydroxyl groups in the 1,2-positions it might be expected to react much like the other compounds of this type.

Eegriwe<sup>2</sup> has found that like alizarin, quinalizarin, rufigallic acid, and anthragallol, flavopurpurin gives a sensitive color reaction with stannic tin. With stannic compounds flavopurpurin yields an orange color similar to that formed with stannic tin and anthrapurpurin. For details of its use, refer to the section on anthrapurpurin (page 440). The test may be made by substituting flavopurpurin for anthrapurpurin in the outlined procedure.

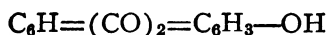
1. O. Frobenius and H. Hepp, *Ber.* **40**; 1049 (1907).
2. E. Eegriwe, *Z. anal. Chem.* **120**, 81-4 (1940); *C.A.* **35**, 48 (1941).

### 1-HYDROXYANTHRAQUINONE

$C_{14}H_8O_3$

Mol. Wt. 224.20

Beil. Ref. VIII, 338.



**Use:** Detection of boric acid, hafnium and zirconium.

1-Hydroxyanthraquinone crystallizes from alcohol as orange-red needles, which are easily soluble in ether and benzene. The compound is insoluble in cold ammonium hydroxide, but is completely soluble in the hot reagent. It does not dissolve readily in 10 per cent aqueous sodium hydroxide. It melts at 200° C., and is somewhat volatile with steam.

**Preparation:** Add 22.3 g. of 1-aminoanthraquinone to a flask containing 130 ml. of concentrated sulfuric acid, and warm on a water bath until dissolved. Cool, and add 8 g. finely powdered sodium nitrite in small quantities, and after each addition cork the flask and shake strongly. Then slowly heat the mixture to 120-130° C. until the evolution of nitrogen has ceased, and a test portion shows the separation of a yellow compound on the addition of water. To obtain an easily filterable precipitate, decompose the warm solution in small quantities with water. Then heat the diluted mass, filter while hot, and wash the residue with hot water until neutral. Dissolve the moist residue in hot 1-2 per cent sodium hydroxide solution, filter, and decompose the filtrate by boiling with hydrochloric acid.<sup>2</sup>

**Detection of boric acid.** Many of the hydroxyanthraquinone dyes react with boric acid in the presence of concentrated sulfuric acid to form colored boric esters or boric-sulfuric esters. This reaction has been utilized in several analytical procedures for boron. Feigl and Krumholz<sup>1</sup> have investigated a number of these hydroxyanthraquinones to determine their analytical possibilities, and their results are shown in Table 59.

**Procedure.** To test for boric acid, mix a dilute solution of the dye in concentrated sulfuric acid with a small quantity of the material to be tested and warm slightly. Compare the resulting color with a sulfuric acid solution of the dye of the same concentration. With boric acid the sulfuric acid solution of 1-hydroxyanthraquinone changes from yellow to orange.

**Detection of hafnium and zirconium.** 1-Hydroxyanthraquinone may be substituted for quinalizarin in a test for hafnium and zirconium<sup>3</sup> (page 467).



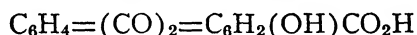
TABLE 59.—REACTIONS OF BORIC ACID WITH HYDROXY-ANTHRAQUINONE DYES

Dye	Color in Conc. $\text{H}_2\text{SO}_4$ without $\text{B}_2\text{O}_3$	Color in Conc. $\text{H}_2\text{SO}_4$ with $\text{B}_2\text{O}_3$
1-hydroxyanthraquinone	Yellow	Orange
2-hydroxyanthraquinone	Red-yellow	Red-yellow
1,2-dihydroxyanthraquinone	Wine-red	Violet
1,3-dihydroxyanthraquinone	Yellow	Yellow
1,4-dihydroxyanthraquinone	Red	Yellow-fluorescent
1,5-dihydroxyanthraquinone	Red	Red-violet
1,8-dihydroxyanthraquinone	Red-yellow	Red
2,3-dihydroxyanthraquinone	Brown	Brown
2,6-dihydroxyanthraquinone	Red	Red
2,7-dihydroxyanthraquinone	Red	Red
Alizarinsulfonic acid	Red-yellow	Red
1,2,3-trihydroxyanthraquinone	Brown	Violet-brown
1,2,4-trihydroxyanthraquinone	Orange	Wine-red
1,4,5,8-tetrahydroxyanthraquinone	Blue	Blue
1,2,5,8-tetrahydroxyanthraquinone	Violet	Blue

1. F. Feigl and P. Krumholz, *Mikrochemie, Pregl Festschrift*. 77 (1929); *C.A.* **24**, 2400 (1930).
2. F. Ullmann and A. Conzetti, *Ber.* **53**, 829 (1920).
3. H. A. Liebhafsky and E. H. Winslow, *J. Am. Chem. Soc.* **60**, 1776-84 (1938); *C.A.* **32**, 7843 (1938).

### 1-HYDROXY-2-CARBOXYANTHRAQUINONE

$\text{C}_{15}\text{H}_8\text{O}_5$  Mol. Wt. 268.21 Beil. Ref. X, (496).



This reagent is a yellow crystalline solid melting at 224-225° C. It is moderately soluble in organic solvents, and is soluble in alkalis and ammonium hydroxide with the formation of a red color. It dissolves in concentrated sulfuric acid to give a yellow to red color.

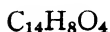
**Preparation:** 1-Hydroxy-2-carboxyanthraquinone is prepared by diazotizing 1-aminoanthraquinone-2-carboxylic acid.<sup>1</sup>

**Reaction with ions.** Updike and co-workers<sup>2</sup> report that 1-hydroxy-2-carboxyanthraquinone gives color changes or precipitates with 53 ions in various tests with inorganic ions at different pH values. The reagent is therefore not sufficiently specific to be of much value as an analytical reagent, but possibly more study may reveal important applications.

1. R. Scholl, *Monatsh.* **34**, 1023 (1913).
2. J. A. Updike, O. W. Clark, Jr., and R. M. Irby, *Va. J. Sci.* **3**, No. 1, 22 (1942); *C.A.* **36**, 3114 (1942).

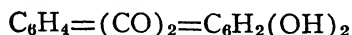
**HYSTAZARIN**

Synonym: Hystazine, 2,3-dihydroxyanthraquinone



Mol. Wt. 240.20

Beil. Ref. VIII, 462.

**Use:** Detection of calcium and magnesium.

This compound occurs as yellow-brown needles having a melting point above  $280^{\circ}\text{C}$ . It is soluble in sulfuric acid, acetic acid, and acetone; but it is insoluble in benzene, and only slightly soluble in ether and hot alcohol. It is soluble in alkalis with the formation of a cornflower-blue color, and in ammonium hydroxide with a violet color.

**Preparation:** Hystazarin is formed with alizarin by heating 30 g. of pyrocatechol with 42 g. phthallic anhydride and 300 g. concentrated sulfuric acid for 30 minutes at  $180^{\circ}$ - $200^{\circ}\text{C}$ . To separate hystazarin from alizarin, mix the sulfuric acid solution with water, remove alizarin by thorough extraction with boiling toluene, and then crystallize the undissolved hystazarin from acetic acid. Hystazarin may also be separated from the easily volatile alizarin by subliming in a vacuum.<sup>2</sup>

**Detection of calcium and magnesium.** A blue, ammoniacal solution of hystazarin turns reddish-violet when added to a solution containing calcium or magnesium salts.<sup>1</sup> This reaction may be used for the detection of calcium and magnesium.

**Reagent.** Dissolve 0.01 g. of hystazarin in 10 ml. of 10 per cent ammonia. This solution decomposes on long standing, and so it should be used shortly after preparation.

**Procedure.** Add a few drops of the hystazarin reagent to the solution to be tested. A reddish-violet color is a positive test.

One ml. of calcium chloride solution containing 0.004 mg. Ca gives a test. The limiting concentration is 1:250,000.

1. F. Feigl, G. Hirsch, and I. Tamchyna, *Mikrochemie*, **7**, 10-20 (1929); *C.A.* **23**, 4421 (1929).
2. C. Liebermann and A. Scholler, *Ber.* **21**, 2501, 2503 (1888).

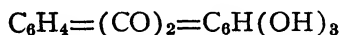
**PURPURIN**

Synonym: 1,2,4-Trihydroxyanthraquinone



Mol. Wt. 256.20

Beil. Ref. VIII, 509.

**Use:** Detection of aluminum, boron, fluoride, hafnium and zirconium.**Determination of fluoride.**

Purpurin occurs as deep red crystals or as orange-yellow crystals with one mole of water. The melting point of the anhydrous compound is  $256$ - $259^{\circ}\text{C}$ . It is

slightly soluble in cold water, and more soluble in boiling water. It is soluble in ethyl alcohol, ether, and toluene.

**Preparation:** Purpurin is prepared by warming gradually 1 part of alizarin with 8-10 parts of concentrated sulfuric acid and 1 part of arsenic acid or manganese dioxide.<sup>1</sup>

**Analytical reactions.** Purpurin may be substituted for alizarin, quinizarin, or other hydroxyanthraquinone dyes having hydroxyl groups in the 1,2-positions in analytical reactions for aluminum, boric acid, fluoride, and zirconium. The reactions are similar in type to those obtained with the more frequently used alizarin, alizarinsulfonic acid, or quinizarin.

**Detection of aluminum.** Purpurin reacts with aluminum salts to form pink to red complexes similar to those formed with alizarin (page 411). This reaction has been used by Kershner and Duff<sup>2</sup> for the detection of aluminum.

**Reagent.** Dissolve 0.4 g. of purpurin and 10 mg. of gum sandarac in 1 liter of ether. Commercial ether is satisfactory. Alcohol tends to diminish the sensitiveness of the reaction somewhat, but the amount present in commercial ether does not prevent the detection of traces of aluminum. The gum sandarac is not very soluble in ether, and so the 10 mg. required for the reagent is most conveniently added by first dissolving in 1 ml. of alcohol. More than 10 mg. of the gum sandarac must be avoided. Sugar, starch, glucose, dextrin, gum tragacanth, gum dammar, and gum copal may be used to replace the gum sandarac as a stabilizer.

**Procedure.** Add N ammonium hydroxide to the solution to be tested until alkaline. Boil to coagulate the precipitate and filter. Wash the precipitate about three times with hot distilled water, and then pour 5 ml. 6 N ammonium hydroxide over the precipitate and collect the filtrate in a clean test tube. Add 10 ml. of N ammonium chloride solution, and 1 ml. of purpurin reagent to the filtrate. Shake well. A pink foam collects above the solution and remains several minutes in the presence of aluminum. Do not shake more than once as this tends to break up the stabilized foam.

There is no interference from elements commonly included in the usual scheme of qualitative analysis. Beryllium, lanthanum, praseodymium, neodymium, cerium, silicic acid, borate, phosphate, fluoride and other anions do not interfere if the above procedure is followed.

The test will detect 0.5 mg. of aluminum in presence of 50 mg. of chromium and iron. The reaction will detect as little as 0.001 mg. aluminum when only minute quantities of other elements are present.

**Detection of fluoride.** Kolthoff and Stansby<sup>3</sup> have studied a method for the determination of fluorides in which purpurin is substituted for alizarinsulfonic acid in a modification of the de Boer-Basart reaction. This method may be applied to both qualitative and quantitative procedures.

**Reagent.** Dissolve 0.16 g. of  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  in 100 ml. of concentrated hydrochloric acid and add 100 ml. of water to insure complete solution.

Dissolve 9 mg. of purpurin in 30 ml. of ethyl alcohol and add the resulting solution slowly and with continuous shaking to the zirconium solution. Finally, add 620 ml. concentrated hydrochloric acid and dilute with water to 1 liter.

It is essential that the purpurin be added to the zirconium solution, since otherwise the solution becomes cloudy. Allow the mixture to stand overnight and then use. The reagent is stable for at least one month.

**Procedure.** In the absence of interfering substances, dissolve the material to be tested in 2 ml. of 6 N hydrochloric acid and then add 2 ml. of the reagent. The pink color of the reagent turns yellow immediately if 0.003 mg. or more of fluoride is present. To confirm the presence of fluoride, add solid zirconium oxychloride, a little at a time, with shaking. If the yellow color is caused by fluoride, the original pink color of the reagent reappears. If it does not, or if a cloudy or orange solution results after the addition of the zirconium-alizarin reagent, the presence of interfering substances which have destroyed the dye is indicated. The final acidity of the mixture should lie between 7 N and 10 N in hydrochloric acid. If the acidity is greater than 10 N, the color in the absence of fluoride is orange or yellow; if less than 6 N, a cloudy solution forms. The test is impossible at an acidity of less than 4 N.

Oxalic acid and sulfuric acid interfere with the test, and phosphates interfere by precipitating zirconium phosphate. Borates alone have no influence on the reaction, but they prevent the formation of the yellow color in the presence of fluorides unless the fluorides are present in excess. Nitrate does not interfere immediately, but upon long standing with nitrates the dye is destroyed. Strongly oxidizing substances, such as chlorates, bromates, and iodates, cause the formation of chlorine, which destroys the dye, but this can be rendered harmless by the addition of sulfurous acid.

Borofluorides and silicofluorides react like fluoride. A distillation method may be used to remove the fluorine from the presence of interfering substances. This method has a sensitiveness of 0.005 mg. fluorine.

**Determination of fluoride.** Purpurin is used in the following procedure for the determination of fluoride:

**Reagents.** *Purpurin reagent:* Dissolve 0.3 g. of purpurin in 1 liter of ethyl alcohol.

*Zirconium chloride solution:* Dissolve sufficient zirconium oxychloride,  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ , in 10 N hydrochloric acid to form a solution containing 0.8 g. of zirconium per liter. Prepare the zirconium solution in small quantities, or standardize frequently, since the chloride settles out on standing.

*Color standard:* Dissolve 19.6 g. of cobalt nitrate,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 0.132 g. of potassium dichromate in 1 liter of water. Keep in a glass-stoppered bottle.

**Procedure.** From 0.5 to 15 mg. of fluoride ion may be determined by the use of purpurin. Add the material to an oil-sample bottle of about 100 ml. capacity. If the sample is solid, add 2 ml. of water or if it is a liquid, use 2 ml., or a larger volume, and make about 10 N with respect to hydrochloric acid and add 2 ml. of water. Then add 5 ml. 10 N hydrochloric acid from a buret and finally 2 ml. of purpurin solution from a pipet.

Measure 40 ml. of the cobalt-dichromate solution from a graduate into a similar oil-sample bottle. This is used as a standard color for comparison. The zirconium solution in hydrochloric acid is now added to the solution of the fluoride sample from a buret until the color of the solution begins to approximate that of the cobalt-dichromate standard. Now add 10 N hydrochloric acid to make the total volume slightly less than 40 ml., and add more of the zirconium solution until the color produced matches that of the standard when the total volume of the solution is 40 ml. (adjust by adding 10 N hydrochloric acid from a buret). The zirconium solution must be added slowly and with shaking so that the titration requires about 1-2 minutes. Calculate the number of mg. of zirconium used and subtract 1 mg. from this amount. The corresponding quantity of fluoride is found by consulting Table 60:

TABLE 60.—FLUORIDE CORRESPONDING TO ZIRCONIUM USED

Mg. of Zr used less 1 mg.	Fluoride present	Mg. of Zr used less 1 mg.	Fluoride present
1	0.40	15	6.63
2	0.75	16	7.15
3	1.20	17	7.73
4	1.60	18	8.26
5	2.00	19	8.90
6	2.47	20	9.50
7	2.90	21	10.10
8	3.25	22	10.72
9	3.70	23	11.40
10	4.15	24	12.08
11	4.65	25	12.90
12	5.10	26	13.70
13	5.60	27	14.53
14	6.12	28	15.40

Colored substances, substances which form free chlorine with hydrochloric acid; phosphates or other substances which precipitate zirconium; substances which form stable complexes with fluoride, such as aluminum and boric acid; and sulfates, oxalates and nitrites interfere. Oxidizing agents may be reduced with a sodium sulfite before titration. Phosphate interferes strongly.

**Detection of zirconium and hafnium.** de Boer has studied the behavior of a number of hydroxyanthraquinone dyes with a view to employing them as possible substitutes for alizarinsulfonic acid in color reactions for zirconium, hafnium and

fluoride.<sup>4</sup> Purpurin, having hydroxyl groups in the 1,2-positions, gives characteristic color reaction with zirconium in much the same manner as alizarinsulfonic acid. The behavior of hafnium with purpurin resembles that of zirconium. In concentrated hydrochloric acid solutions the color fades sooner with hafnium than with most of the hydroxyanthraquinone dyes. Hafnium stands between zirconium and thorium, but closer to zirconium in this respect, since thorium gives stronger colorations in almost neutral solutions that fade even in dilute hydrochloric acid.

**Detection of boric acid.** Purpurin, like other hydroxyanthraquinone dyes, gives characteristic color reactions with boric acid in the presence of concentrated sulfuric acid.<sup>5</sup> This color is due to the formation of boric or boric-sulfuric esters. The color change is from orange to wine-red with purpurin. The limit of identification is 6γ of boron. Nitrates, arsenites, fluorides, and oxidizing agents, such as chromic and hydroferricyanic acid, interfere. For details of this method, refer to the procedure with quinalizarin (page 465). Purpurin is less sensitive than quinalizarin.

1. De Lalande, *Compt. rend.* **79**, 669; *Bul. soc. chim.* [2], **22**, 425; *Jahr. Fortsch. Chem.* **486** (1874).
2. K. Kershner and R. D. Duff, *J. Chem. Ed.* **9**, 1271-3 (1932); *C.A.* **26**, 4007 (1932).
3. I. M. Kolthoff and M. E. Stansby, *Ind. Eng. Chem. Anal. Ed.* **6**, 118-21 (1934); *C.A.* **28**, 2643 (1934).
4. J. H. de Boer, *Rec. trav. chim.* **44**, 1071-6 (1925); *C.A.* **20**, 1042 (1926).
5. F. Feigl and P. Krumholz, *Mikrochem., Pregl Festschr.* **77-86** (1929); *C.A.* **24**, 2400 (1930).

## QUINALIZARIN

Synonym: 1,2,5,8-Tetrahydroxyanthraquinone, alizarin cyanin  
3R(By), alizarin bordeaux

$C_{14}H_8O_6$

Mol. Wt. 272.20

Beil. Ref. VIII, 549.



**Use:** Detection of aluminum, beryllium, boron, calcium, cerium, gallium, germanium, indium, lanthanum, magnesium, neodymium, phosphate, praseodymium, scandium, thallium, thorium, tin, zirconium.

Determination of aluminum, beryllium, boron, fluoride, gallium, hafnium, indium, magnesium, phosphate, scandium, zirconium.

Quinalizarin occurs as red, rhombic needles, which possess a green metallic luster. The compound is insoluble in water and is only slightly soluble in ethyl alcohol and ethyl ether, but it dissolves readily in alkaline solutions with the formation of a violet color, and in sulfuric acid to yield a bluish-violet solution. It melts above 275° C., and sublimes at its boiling point.

**Preparation:** Slowly add 5 g. of dry, powdered alizarin to 50 g. fuming sulfuric acid (70 per cent  $SO_3$ ) so as to avoid too great an increase in temperature. Allow the mixture to stand 24-48 hours at 35-40° C., or until a sample poured

into ice water and made alkaline with sodium hydroxide gives a yellowish-red solution. Then pour into 100 g. of concentrated sulfuric acid, and pour this mixture onto ice. Dissolve the precipitate in sodium hydroxide and acidify with sulfuric acid. Avoid too great an excess of acid. Boil until a precipitate forms, filter, wash, distill, and crystallize from nitrobenzene.<sup>2</sup>

**Analytical reactions.** In 1924 Hahn, Wolf and Jager<sup>1</sup> suggested the use of the dye quinalizarin as a reagent for the detection of magnesium, and since that time it has been used for the detection and determination of many other substances. Because of their similarity in structure alizarin and quinalizarin react in much the same manner with magnesium, beryllium, aluminum, boric acid, fluorides, zirconium, indium, gallium, germanium, thallium, hafnium, lanthanum and other ions. The compounds which are formed are generally adaptable to the detection and colorimetric determination of the above substances.

**Detection of magnesium.** An alkaline solution of quinalizarin changes in color from reddish-violet to a cornflower blue in the presence of as little as 0.001 mg. of magnesium ion in one ml. of solution. This color change, which is due to the formation of a lake, is most effectively observed against a silver-colored background. Larger quantities of magnesium yield a blue precipitate. The composition of the colored compound has not been determined, but it is probably an adsorption complex of magnesium hydroxide and the dye. The behavior of the dye in the presence of magnesium has been made the basis for methods for the detection and determination of small quantities of magnesium.<sup>1,3-6</sup>

Cervinka<sup>7</sup> performs the test as follows:

**Reagent.** Dissolve 10 mg. of quinalizarin in 100 ml. of ethyl alcohol.

**Procedure.** Add 2 ml. of the reagent to 2 ml. of the solution to be tested, and then add dropwise 1 ml. of 2 N sodium hydroxide. In the presence of magnesium the violet-red solution turns blue; and large quantities of magnesium give a blue flocculent precipitate. The color does not form immediately at low concentrations of magnesium, but on standing, or after heating, the color may appear at dilutions corresponding to 0.001 N  $\text{MgSO}_4$ .

By means of a refined technique Hahn<sup>8</sup> has been able to identify 0.001γ magnesium in a microdrop.

Hahn<sup>1</sup> has suggested the use of two reagents for detecting magnesium: one, consisting of 10-20 mg. of the dye in 100 ml. of ethyl alcohol, is used with small amounts of magnesium; and the other, which is a freshly prepared solution of the dye in 2 N ammonium hydroxide or sodium hydroxide, is used for larger quantities of magnesium.

Quinalizarin, while useful, is not as sensitive nor as specific as 8-hydroxyquinoline, Titan yellow, 5-*p*-acetaminophenylazo-8-hydroxyquinoline, or *p*-nitrobenzeneazoresorcinol.

In the presence of calcium chloride, calcium hydroxide, strontium chloride, barium chloride, or barium hydroxide, quinalizarin gives color shades almost identical with those caused by magnesium. The latter may, however, be de-

tected in the filtrate from which calcium, barium, and strontium have been precipitated.<sup>7</sup> According to Okac,<sup>9</sup> Hahn's reagent is added to a solution which has previously been treated with ammonium carbonate to separate magnesium and alkalis from other metals. Under these conditions the reagent is useful for detecting small quantities of magnesium, but it is not to be regarded as specific. All attempts to make the reagent more specific for magnesium have failed. Attempts to separate the magnesium compound from those of calcium, strontium, and barium by using organic solvents have also been unsuccessful.

A blue color is also formed when quinalizarin is added to a solution, of zinc chloride, but this color disappears in a comparatively short time. Aluminum chloride and beryllium chloride also give blue colors with the reagent. The sensitivity of the magnesium reaction appears to be markedly diminished by the presence of zinc or aluminum. In testing for small amounts of magnesium in the presence of large quantities of aluminum, the latter must be kept in solution by using an excess of sodium hydroxide, or by the addition of a tartrate. Ammonium salts and phosphoric acid also decrease the sensitiveness of the test and should be removed. Ammonium salts are best removed by ignition. Lanthanum, neodymium, praseodymium, cerium, zirconium, and thorium salts react with quinalizarin in much the same manner as magnesium. Beryllium salts react in a similar manner, but the beryllium compound with quinalizarin is differentiated from the magnesium compound by its stability toward oxidizing agents; in a sodium hydroxide solution bromine destroys the blue beryllium compound while the color of the magnesium lake is unchanged.<sup>10</sup>

Flood and Smedsaas<sup>44</sup> and Venturello<sup>45</sup> have used quinalizarin as a developer for the chromatographic detection of magnesium. As the developer, Venturello recommends the use of a 0.5 per cent solution of quinalizarin in 0.2 N sodium hydroxide. After washing out the column with distilled water, and a preliminary treatment with 0.2 N sodium hydroxide solution, the developing solution is added to the adsorption tube.

Cauer and Cauer<sup>53</sup> have used quinalizarin for the detection of magnesium in fog particles. The reagent has also been used for the microchemical detection of magnesium as an impurity in ammonium molybdate.<sup>57</sup>

**Determination of magnesium and phosphate.** Hahn and Meyer<sup>11</sup> have reported that a very slight excess of phosphate in an ammoniacal solution saturated with magnesium ammonium phosphate turns quinalizarin reddish, while a slight excess of magnesium ion causes a blue color. A fairly accurate method for determining either phosphate or magnesium has been based on these color changes. The principal difficulty depends upon the ability of the operator to obtain an exactly normal precipitate of  $\text{MgNH}_4\text{PO}_4$ . Since the dye acts as an indicator, the titration to  $\text{MgNH}_4\text{PO}_4$  is possible.

Thiel and von Hengel<sup>12</sup> have proposed the use of the quinalizarin-magnesium color reaction as the basis for a colorimetric method for determining magnesium. A blue precipitate is likely to form, but this can be prevented by the addition of gum arabic. The latter is likely to contain some magnesium, and so must be purified by extraction with alcohol and evaporation of the resulting solution. The blue color is stable for several months. Beryllium, the rare earth metals,



thorium, and zirconium also give a blue color with quinalizarin in a strongly alkaline solution.

**Procedure.** Transfer the neutral or slightly acid sample solution, which should contain not more than 0.3 mg. of magnesium, to a 50-ml. volumetric flask. Add 5 ml. of a 5 per cent aqueous solution of magnesium-free gum arabic. The gum arabic may be omitted if the magnesium concentration is low. Then add 5 ml. of a 0.01 per cent solution of quinalizarin in 96 per cent ethyl alcohol, and dilute with water to 35-40 ml. Next add 5 ml. of 2 N sodium hydroxide, and dilute to the mark. Measure the extinction at 600 m $\mu$ . Make the measurement soon after mixing, since the excess quinalizarin is not stable in an alkaline medium.

Methods have been reported for determining magnesium in aluminum alloys,<sup>8</sup> copper-zinc alloys,<sup>13</sup> and in plant materials.<sup>14</sup>

**Detection of calcium.** Pavelka and Setta<sup>57</sup> have used quinalizarin for the microchemical detection of calcium as an impurity in ammonium molybdate. The reaction is similar to that obtained with magnesium.

**Detection of beryllium.** A violet, alkaline solution of quinalizarin gives a beautiful blue color or precipitate when added to an alkaline solution of a beryllium salt. This reaction is suitable for detecting beryllium in the absence of interfering substances. The test is performed as follows:<sup>10</sup>

**Procedure.** Add a few drops of a 5 per cent solution of quinalizarin in 0.25 N sodium hydroxide to 10 ml. of the solution to be tested, and then make alkaline with 0.25 N sodium hydroxide. Compare the resulting color with a blank test on a solution containing a pure alkali. Sodium hydroxide alone gives a violet color, while the beryllium test is blue.

Magnesium gives a similar test, but the magnesium lake can be distinguished from that of beryllium as described in the test for magnesium (see above).

The quinalizarin reaction may be used as a spot test for beryllium.

**Reagent.** Use a saturated alcoholic solution of quinalizarin or a freshly prepared solution of 0.05 g. quinalizarin in 100 ml. 0.1 N sodium hydroxide.

**Procedure.** Mix 1 drop of solution to be tested on spot plate with a drop of the freshly prepared solution of quinalizarin in sodium hydroxide. If the quantity of beryllium is small, use the alcoholic solution. After mixing, add 1 drop of ammonium hydroxide or sodium hydroxide. A blue color indicates the presence of beryllium.

The limit of identification is 0.14 $\gamma$  beryllium at a concentration of 1:353,000.

Quinalizarin also gives sensitive reactions with neodymium, praseodymium, cerium, lanthanum, zirconium and thorium.<sup>5</sup> Consequently, the test for beryllium cannot be successfully employed in the presence of these metals. The beryllium test is disturbed by the presence of ammonium salts, which must be removed. Aluminum, lead, zinc, and antimony salts do not interfere. Copper and nickel

salts interfere because of their color, but they may be decolorized by the addition of potassium cyanide. Any interference by ferric iron may be removed by the addition of tartrates, but in the presence of aluminum, tartrates interfere due to the formation of a red color in the alkaline solution of quinalizarin. Phosphates should be absent. The quinalizarin test is very satisfactory when applied to solutions of a beryllium salt that has been purified either by extraction with ethyl ether or by sublimation.<sup>16</sup>

A microchemical method which will detect 0.14 $\gamma$  of beryllium is described by Dubsky and Krametz.<sup>17</sup> Quinalizarin has also been used in the qualitative analysis of the arsenic and iron groups.<sup>18,19</sup>

Reinacker<sup>20</sup> uses Fischer's method to detect beryllium in minerals.

**Determination of beryllium.** A number of methods have been devised for determining beryllium by means of the blue color which it yields with quinalizarin.

Beryllium may be titrated directly with a standard quinalizarin solution with the end-point indicated by the color change produced by an excess of quinalizarin. One mole of quinalizarin unites with 2 moles of beryllium.<sup>21</sup> An excess of quinalizarin reagent may be added to an unknown beryllium solution, and the excess titrated with standard beryllium solution to a clear, pure blue end-point. As little as 0.1 mg. of beryllium can be determined in this way.<sup>10</sup> Small quantities of beryllium can be determined by precipitating with an excess of an ammoniacal solution of quinalizarin, centrifuging the precipitate, and estimating the excess quinalizarin colorimetrically.

Quinalizarin yields a blue color with beryllium in a sodium hydroxide solution, but in the absence of beryllium the dye has a violet color. Thus, beryllium can be determined by a mixed-color method by treating the alkaline solution with a sufficient excess of reagent to form a blue-violet color whose hue can be matched by a standard series method or by a colorimetric titration.<sup>10,22</sup>

Aluminum does not interfere, even if present in comparatively large quantities, and in general neither do those metals whose hydroxides are soluble in excess sodium hydroxide. Relatively large quantities of zinc, however, also give a blue color. Metals whose hydroxides are insoluble in excess sodium hydroxide must be absent. Magnesium and iron especially interfere. Zirconium, thorium, and the rare earths in low concentrations yield blue colors with quinalizarin. Interference by copper, nickel, and zinc may be eliminated by the addition of potassium cyanide. Calcium prevents the color change of quinalizarin by beryllium, while barium gives a similar color change, although of less intensity.<sup>23</sup> Iron, when present in quantity greater than that of beryllium, interferes with the colorimetric titration.<sup>24</sup> Phosphate does not interfere.

The concentration of sodium hydroxide influences the hue of the solution, and substances such as ammonium salts which change the pH of the solution must be present only in small quantities.

The color comparison should be made as soon as possible after the addition of the quinalizarin, since there is a slow fading of the color due to the instability of the reagent in a strongly alkaline solution.

**Reagent.** Shake 10 mg. of finely powdered quinalizarin with 100 ml. of acetone until almost all of the solid has dissolved. Decant the clear supernatant liquid and store in the dark.

**Procedure.** To 5-10 ml. of the solution containing 1-5 $\gamma$  of beryllium, add sufficient sodium hydroxide solution to make the concentration 0.2-0.3 N. If a relatively large quantity of aluminum is present, increase the concentration of sodium hydroxide to 0.5 N. Prepare a series of standards having the same volume and the same concentration of sodium hydroxide as the unknown. To both standards and unknown add 1.0 ml. of the quinalizarin solution and compare immediately. The comparison is conveniently carried out in 1.8  $\times$  15 cm. flat bottom tubes.

The comparison may be made by colorimetric titration. A 0.005 per cent beryllium solution is added from a microburet to a solution having the same volume as the unknown and containing the same quantities of quinalizarin and sodium hydroxide until the hues of the two solutions match.

**Detection of aluminum.** In a weakly acid solution, quinalizarin reacts with aluminum to give a violet-purple lake, which flocculates on long standing. Magnesium and beryllium may also give colored lakes with quinalizarin, but in the presence of sodium hydroxide a lake is obtained only with magnesium, while the beryllium and aluminum remain in solution. Beryllium may, however, give a precipitate in the presence of considerable ammonium salts. Aluminum, on the other hand, is determined in a faintly acid solution without interference from either beryllium or magnesium.

The aluminum-quinalizarin reaction is used for the detection and determination of aluminum. The test is carried out as follows:<sup>25</sup>

**Procedure.** To 10 ml. of neutral solution to be tested, add 0.25-1.0 ml. of a buffer prepared by mixing 10 parts of 5 N acetic acid and 9 parts of 5 N ammonium hydroxide (pH 5.4-5.8 on 10-fold dilution), and 0.3 ml. of 0.1 per cent alcoholic quinalizarin solution. Shake well and allow to stand about 20 minutes. Observation may be made immediately by heating to 50° C.

The color of the solution varies from an intense violet for 1 mg. of aluminum per liter to a faint violet for 0.1 mg. per liter, and it can be used to detect 0.02 mg. aluminum per liter.

The reaction is not influenced by alkali metals, alkaline earths, zinc, magnesium, nickel, cobalt, cadmium, lead, or chromic salts. Copper and iron are objectionable because of the color of solutions of their salts. Antimony, tin, and bismuth give precipitates with quinalizarin at the required pH, but this interference may be eliminated by the addition of a tartrate.

Hahn<sup>26</sup> has made the quinalizarin reaction the basis for a sensitive spot test for aluminum:

**Reagent.** Dissolve 10 mg. of quinalizarin in 2 ml. of pyridine and dilute with 20 ml. of acetone. Immerse filter paper in this solution and allow to dry.

**Procedure.** Filter paper which has been impregnated with the above solution and dried has about the same color as neutral litmus, and acts like litmus when treated with acids and bases. Aluminum tends to prevent this change of color, so that test paper which has been moistened with a solution containing aluminum shows a characteristic appearance when treated with ammonia and acetic acid. When the paper is held for a time in ammonia fumes, the treated spot remains redder than the rest of the paper, and when held in acetic acid the spot remains bluer. This test is modified by holding the paper in ammonia fumes and then over glacial acetic acid until the blue color disappears and the untreated paper remains brown (color of the free quinalizarin). The spot remains violet or red according to the amount of aluminum originally present. This test may be obtained with 0.005% aluminum in 0.1 ml.

Thanheiser<sup>27</sup> has developed a test for aluminum in steel by using a drop of the solution obtained when 1-2 drops of a mineral acid is applied to the freshly cleaned surface of a piece of steel. The test is performed as above.

**Determination of aluminum.** In a faintly acid solution aluminum forms a violet-purple lake with quinalizarin. From 0.02-0.5 mg. of aluminum may be determined colorimetrically according to the method of Kolthoff:<sup>25,26</sup> 27

**Reagents.** *Quinalizarin solution:* Dissolve 0.1 g. of quinalizarin in 100 g. of ethyl alcohol.

*Buffer solution:* A buffer solution is prepared by mixing 10 volumes of 5 N acetic acid and 9 volumes of 5 N ammonium hydroxide.

**Procedure.** To 10 ml. of solution containing 0.02-1.0 mg. of aluminum per liter, add 0.25-1.0 ml. of buffer solution and 0.3 ml. of the quinalizarin reagent. Comparison may be made after 15-20 minutes in cold or immediately after heating. Compare with a blank and with standard aluminum solutions. The color varies from an intense violet with 1.0 mg. aluminum per liter to a faint violet with 0.1 mg. per liter. As little as 0.02 mg. of aluminum per liter may be detected.

The reaction is not influenced by alkali metals, alkaline earths, zinc, magnesium, nickel, cobalt, cadmium, lead, or chromic salts. Copper and iron are objectionable because of their color. The disturbing effect of copper may be removed by the addition of an excess of sodium thiosulfate. Antimony, tin and bismuth yield precipitates at the required pH, but these metals, and also iron, do not interfere in the presence of Rochelle salt or sodium tartrate. The sensitiveness of the reaction is diminished by this treatment. Schams<sup>50</sup> has used quinalizarin for the determination of aluminum in plants.

**Detection of gallium.** Quinalizarin reacts with solutions of gallium salts to give a pink to amethyst color depending on the pH of the solution and its gallium content. The test is performed as follows:<sup>28,29</sup>

**Reagent.** Use a freshly prepared 0.01 per cent solution of quinalizarin in ethyl alcohol.

**Procedure.** Make the solution 0.5 N in ammonium chloride, and 1 N in ammonium acetate to intensify the color. Adjust the pH to 5.0, and add sodium fluoride until the concentration corresponds to 0.5 g. sodium fluoride per liter. When the reagent is added to this solution, as little as 0.02 mg. of gallium in 1 liter can be detected.

Not more than 10 mg. of aluminum or 1 mg. of iron should be present, and both vanadium and molybdenum must be absent. Zinc decreases the sensitiveness of the test. Indium and thallium also give a positive test. Phosphate decreases the color given by gallium.

Under the conditions outlined above for the gallium test, the following ions also give color reactions:

Ferric, stannous, antimonous, cupric, lead (ous), indium, germanium (IV), vanadyl, vanadate, and molybdate give colors which are not completely inhibited by fluoride. Ferric and lead (ous) ions yield blue colors, while the other ions cause a pink color. All reactions are very sensitive.

Zirconium and thorium and the rare earths give blue, while stannic, beryllium, aluminum, thallic, titanium, arsenite, and antimonate cause a pink color which can be prevented by the addition of fluorides.

Alkalies, alkaline earths, magnesium, manganous, ferrous, mercuric, thallous, cadmium, uranyl, tungstate, and arsenate ions yield no color.

Silver, mercurous bismuth, tantalic, and columbic ions either precipitate as chlorides or hydrolyze and cause no interference after filtration.

Cobaltous, nickel, and chromium ions do not interfere except for their color. Zinc may be present to the extent of 0.5 g. per liter. More than this gives an amethyst color.

Citrate, oxalate and tartrate prevent color formation in all cases.

Morin gives the most sensitive test for gallium, but quinalizarin is reported as nearly as good.<sup>30</sup>

**Determination of gallium.** Gallium may be determined colorimetrically by means of the color reaction with quinalizarin.<sup>32</sup> The best concentrations for color comparisons in Nessler tubes lie between 0.02 and 0.2 mg. gallium per liter. Tin, antimony, indium, platinum, and germanium also form lakes with the reagent. Vanadium and molybdenum must be absent, and not more than 10 mg. of aluminum or 1 mg. of iron may be present.

Because of many common interferences, various procedures must be used for determining gallium in the presence of different ions.

(a) **In the presence of aluminum.** If less than a few mg. of potassium or 100 mg. of sodium is present, proceed as follows:

**Reagent.** Use a 0.01 per cent alcoholic solution of quinalizarin. Best results are obtained if the solution is from one to four days old. Discard after one week.

**Procedure.** Add dilute ammonium hydroxide to the sample solution to the appearance of a turbidity, then add 6 N hydrochloric acid until clear,

and then add 4 ml. in excess. Add 7.7 g. of ammonium acetate and 2.7 g. of ammonium chloride and dilute to 70-80 ml. Heat to 70-80° C. and add with stirring sufficient saturated aqueous sodium fluoride solution to convert all aluminum to  $\text{Na}_3\text{AlF}_6$  and leave an excess of 0.5 g. per liter. Allow to stand 1 hour with occasional stirring, add a little filter paper pulp and filter. Wash with small portions of water containing a few drops of sodium fluoride solution.

Dilute the filtrate to almost 100 ml., adjust the acidity to pH 5.0 and dilute to 100 ml. Transfer an aliquot containing 1-10% of gallium to a 50-ml. Nessler tube. Prepare a series of standards containing the same quantities of sodium acetate, ammonium chloride and sodium fluoride as the unknown. Make the pH the same, and to both unknown and standards add 1.0 ml. of quinalizarin solution. Mix, allow to stand 1-2 minutes and compare.

A preliminary separation of aluminum is unnecessary if the aluminum concentration is less than 15 mg. per liter.

(b) **In the presence of iron and indium.** In the presence of not more than 1 mg. of ferric iron and 100 mg. of indium, proceed as follows:

**Reagent.** Same as in above procedure.

**Procedure.** The volume of the unknown solution should not exceed 25 ml. Heat to boiling and add sufficient 4 N sodium hydroxide solution to make the final concentration 0.5-1 N. Boil until the precipitate is coagulated and add filter paper pulp that has been thoroughly washed with hot 1.5 N sodium hydroxide solution. Filter and wash the precipitate with a hot 1 per cent sodium chloride solution that has been made alkaline with sodium hydroxide. Heat the filtrate nearly to boiling and add 0.5 ml. of 1 per cent potassium permanganate solution, and then add 0.5 ml. of ethyl alcohol. Heat until the green color disappears and a precipitate of manganese dioxide is formed. Filter and wash as above.

Add hydrochloric acid to the filtrate until neutral to litmus, and then add sufficient ammonium acetate, ammonium chloride and sodium fluoride to make the pH of the solution 5.0 and the salt content the same as that recommended in the preceding section. Determine gallium as above.

If the concentration of indium is less than 8 mg. per liter, a preliminary separation is not necessary.

(c) **In the presence of aluminum and iron.** In the presence of both iron and aluminum, proceed as follows:

**Reagent.** Same as above.

**Procedure.** Separate iron as described above and acidify the filtrate with hydrochloric acid. Precipitate aluminum and gallium by the addition of a slight excess of ammonium hydroxide. Filter through a Gooch crucible containing a layer of purified anthracene or phenanthrene. Do not use paper. Transfer the anthracene mat and precipitate to the beaker in which the precipitation was originally carried out, and dissolve the hydroxides by boiling with 6 N hydro-

chloric acid. Filter through a small filter paper previously washed thoroughly with hot 6 N hydrochloric acid. Precipitate the aluminum in the filtrate and proceed as described above.

(d) In the presence of lead, copper, tin, antimony, germanium and platinum.

**Procedure.** Make the solution strongly acid with hydrochloric acid and boil to remove germanium. Reduce the acidity of the solution until hydrolyzable metals just stay in solution, and then add a small excess of pure 60-mesh cadmium metal. Stir until precipitation is complete and filter. Add 2 ml. of concentrated sulfuric acid and evaporate to fumes. Dissolve the residue in 75-100 ml. of water and remove cadmium by electrolysis. Treat the remaining solution with hydrogen sulfide, filter, and treat the filtrate as described above.

The results obtained by determining gallium with quinalizarin in the presence of various ions are given in Table 61, which is taken from the work of Willard and Fogg.<sup>28</sup>

TABLE 61.—DETERMINATION OF GALLIUM WITH QUINALIZARIN

Foreign metal mg.		Gallium Used $\gamma$	Gallium Found $\gamma$
Aluminum	10	0.0	0.0
Aluminum	10	5.0	4.7
Aluminum	10	10	11
Aluminum	20	10	7.5
Iron	0.5	10	9
Iron	1.0	20	20
Iron	2.0	10	5
Indium	100	10	11
Zinc	25	5	6
Zinc 20, Iron 1.0		5	4
Aluminum 15, Iron 1.0		10	8
Lead	100	10	12
Copper	100	10	10
Tin	100	50	53
Germanium	30	10	8

**Detection and determination of indium.** Quinalizarin forms a violet lake with indium, and this reaction is useful for the detection and determination of indium.<sup>29</sup> The test is carried out as follows:

**Procedure.** To 1 ml. of a neutral solution suspected of containing indium (or gallium or thallium) add 1 ml. of a saturated solution of ammonium chloride, and 5-10 drops of a solution prepared by dissolving 0.5 g. of quinalizarin in 10 ml. of concentrated ammonium hydroxide. There is immediate precipitation with 0.7 $\gamma$  of indium in 1 ml. of solution.

If aluminum and zinc are present the sensitiveness of the reaction is decreased.

Indium may be detected in flue dust by a method proposed by von Stein:<sup>31</sup>

**Procedure.** Digest the sample with concentrated sulfuric acid for 10 minutes and evaporate to fumes. Filter, and add water to the filtrate. Neutralize the filtrate to litmus and add a drop of the solution to a strip of filter paper that has been impregnated with a saturated alcoholic solution of quinalizarin. Hold the paper over ammonium hydroxide to form a violet-colored quinalizarinate, and then agitate the paper in hot, saturated boric acid solution. In this way a red or violet lake is obtained. Interfering ions can be masked by adding sodium fluoride and potassium cyanide to the solution of the sample.

In this way indium may be detected in the presence of aluminum, zinc, nickel, cobalt, manganese, beryllium, zirconium and thorium. This test is more sensitive than the analogous reaction with alizarin.

**Detection of scandium.** The blue coloration or precipitate which scandium gives with quinalizarin may be used for the detection of the metal. This reaction is analogous to that with magnesium and beryllium.<sup>32</sup>

**Detection and determination of boron.** Quinalizarin yields a violet color when dissolved in concentrated sulfuric acid, and this color changes to blue when a little boric acid is added.<sup>33</sup> The test is performed as follows:

**Procedure.** Warm a 0.01 per cent solution of quinalizarin in concentrated sulfuric acid with a little of the substance to be tested, also dissolved in 1 ml. of concentrated sulfuric acid.

Smith<sup>34</sup> suggests using a solution of quinalizarin in 93 per cent sulfuric acid. About 0.002g of boron can be detected by this reaction. Fluorides and oxidizing agents, such as nitrate and ferricyanide interfere and must be absent when making the test for boron. Germanic acid gives a similar reaction.

The color of the boric ester is also used for determining boron.<sup>34</sup> This method may be used for the determination of 0.005-0.250 mg. boric acid. The color may be satisfactorily measured with a Lovibond tintometer.<sup>35</sup>

About 2g of boron is the most suitable quantity for measurement. The concentration of the sulfuric acid is important. With more than 4g of boron the sensitiveness of the reaction diminishes in very concentrated sulfuric acid, but with 89 per cent sulfuric acid the reaction is fairly satisfactory. Boron may be determined in plants and soils by this method.<sup>36,43</sup>

Rudolph and Flickinger<sup>46,49</sup> and others<sup>54-56</sup> have proposed the use of quinalizarin for the colorimetric determination of boron in steel. According to this method, the steel is dissolved in 7 N sulfuric acid, and the boron then determined in the usual manner.

Dickinson<sup>47</sup> has proposed a method for determining boron colorimetrically by comparing the color formed with alizarinsulfonic acid with a series of standards prepared with methyl orange. Quinalizarin may be substituted for alizarinsulfonic acid in this procedure, although the colors can be matched more readily with the latter reagent. For details of the procedure, see the section on alizarinsulfonic acid (page 432).

**Detection of germanium.** Germanic acid gives with quinalizarin a reaction similar to that of boric acid. This reagent is more satisfactory than



*p*-nitrobenzeneazochromotropic acid,<sup>37</sup> which is also used for the detection of germanium.

**Detection of thallium.** Thallium yields a lake with quinalizarin, but the test is not especially sensitive.<sup>29</sup> One mg. of thallium may be detected by using the procedure described above for indium.

**Detection of lanthanum.** Lanthanum gives a reaction similar to that of magnesium, and may be detected by the procedure outlined in the section on magnesium.

**Detection of phosphate.** For detection of phosphate, see section on magnesium (page 456).

**Detection of the rare earths.** Sensitive tests may be obtained with neodymium, praeodymium, cerium, lanthanum, zirconium and thorium using quinalizarin:<sup>15</sup>

**Procedure.** To 2 ml. of the solution to be tested, add 10 drops of a 0.005 per cent alcoholic solution of quinalizarin and 5-10 drops of 2 N sodium hydroxide, according to the quantity of the ion present. There appears a more or less intensive blue color with the gradual separation of a precipitate of the same blue color.

Limit of Identification	Concentration Limit
Nd 0.5 $\gamma$ in 1 ml.	1:2 million
Pr 1.06 $\gamma$ in 1 ml.	1:940,000
Ce 1.13 $\gamma$ in 1 ml.	1:870,000
La 2.00 $\gamma$ in 1 ml.	1:500,000
Zr 6.30 $\gamma$ in 1 ml.	1:160,000
Th 6.60 $\gamma$ in 1 ml.	1:151,000

These tests may be carried out as spot tests, which are quite sensitive.

**Procedure.** Place a drop of the test solution on filter paper, which must be free of magnesium, and then spot with a drop of a 0.05 per cent solution of quinalizarin in 0.5 N sodium hydroxide. Then add a drop of 2 N potassium hydroxide. In the presence of the rare earth metals, flecks of more or less intense blue appear.

Limit of Identification	Limiting Concentration
Nd 0.054 $\gamma$ in 1 ml.	1:500,000
Pr 0.067 $\gamma$ in 1 ml.	1:470,000
Ce 0.070 $\gamma$ in 1 ml.	1:435,000
La 0.126 $\gamma$ in 1 ml.	1:238,000
Zr 0.370 $\gamma$ in 1 ml.	1:80,000
Th 0.180 $\gamma$ in 1 ml.	1:151,000

It will be observed that the spot tests are less sensitive than these carried out in test tubes, but smaller quantities may be detected.

In a critical review of the various methods which have been proposed for the detection of thorium, Wenger and Duckert<sup>48</sup> recommend that quinalizarin be used only to confirm the presence or absence of thorium when no other substances are present. The reactions of quinalizarin are too general to be of much value in testing for thorium in the presence of all elements.

**Determination of fluorides.** Quinalizarin appears to have certain advantages over alizarin when used as in the de Boer method (page 414) for the determination of fluorine. It is more sensitive to small changes in fluoride concentration, and the change in color is easier to distinguish.<sup>38</sup>

**Reagent.** Add 5 ml. of 0.14 per cent quinalizarin solution in 0.3 per cent sodium hydroxide to 5 ml. of 0.87 per cent aqueous zirconium nitrate solution and dilute to 400 ml.

**Procedure.** Precipitate sulfates by the addition of 5 ml. of 2 per cent barium chloride solution to 100 ml. of the sample. Allow to stand for several hours and draw off a 50-ml. portion for the determination. Filter if necessary. Add 3 ml. of 1:1 hydrochloric acid and 5 ml. of the reagent solution and mix thoroughly. Allow to stand for 20 minutes and compare with standards that have been similarly and simultaneously prepared.

The fading of the color is a function of time, temperature, and acidity, as well as of fluoride concentration. The best concentration range for the determination is from 0-0.1 mg. of fluorine per 50 ml. of solution.

0.2 p.p.m. of aluminum, 10 p.p.m. of iron, 0.3 p.p.m. phosphate, and 20 p.p.m. of sulfate interfere or make the determination impossible. If aluminum and phosphate are present, the distillation method of Boruff and Abbott<sup>39</sup> is necessary.

Freis and Lauckner<sup>40</sup> have used both alizarinsulfonic acid and quinalizarin as an indicator in the titration of fluoride by means of thorium nitrate (see section on alizarinsulfonic acid).

**Determination of zirconium and hafnium.** By means of a photoelectric recording spectrometer, it is possible to determine zirconium and hafnium by means of the colored lake which they form with quinalizarin.<sup>41</sup>

Other cations may be present in small quantities, but it is impossible to differentiate between hafnium and zirconium.

**Detection of tin.** Quinalizarin, as well as other hydroxyanthraquinone dyes, gives a sensitive color reaction with stannic tin. This test is described in the section on anthrapurpurin (page 440).<sup>42</sup>

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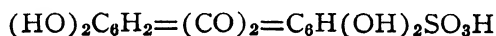
## RUFIANIC ACID

Synonym: Quinalizarinsulfonic acid, alizarin Bordeaux sulfonic acid

$C_{14}H_8O_9S$

Mol. Wt. 352.26

Beil. Ref. XI, 364.



**Use:** Detection of boric acid.

Rufianic acid dissolves in water with the formation of an orange solution. This solution is colored violet by sodium carbonate and blue by sodium hydroxide. The compound is also dissolved in concentrated sulfuric acid to form a blue-red solution.

**Preparation:** Rufianic acid is prepared from quinalizarin by heating with fuming sulfuric acid (30 per cent  $SO_3$ ) in the presence of boric acid at  $130^\circ C$ . until the material becomes water soluble.

**Detection of boric acid.** Rufianic acid gives a red color with boric acid in the presence of concentrated sulfuric acid.<sup>1</sup>

**Reagent.** Dissolve 10 mg. of rufianic acid in 10 ml. concentrated sulfuric acid.

**Procedure.** Add 1 ml. of the reagent to 1-2 drops of boric acid solution. A red fluorescence is a positive test. The test is sensitive to 1:100,000. With 0.2 ml. of solution a limit of identification of 0.2 $\gamma$  boric acid is possible.

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**RUFIGALLIC ACID**

Synonym: Rufigallol, 1,2,3,5,6,7-hexahydroxyanthraquinone

$C_{14}H_8O_8$

Mol. Wt. 304.20

Beil. Ref. VIII, 567.



**Use:** Detection of fluoride, hafnium, tin and zirconium.

Rufigallic acid is a red crystalline compound. It sublimes on heating with partial carbonization. It is insoluble in water, sparingly soluble in alcohol and ether, but soluble in alkali hydroxides with the formation of violet-colored solutions. It also dissolves in sulfuric acid with a red color.

**Preparation:** Rufigallic acid is prepared by heating gallic acid with concentrated sulfuric acid<sup>3</sup> or by heating 1 part of dried gallic acid with 5 parts concentrated sulfuric acid on a water bath and pouring the resulting solution into water.<sup>4</sup>

**Detection of fluoride, tin, hafnium and zirconium.** Rufigallic acid is a hydroxyanthraquinone dye having hydroxyl groups in the 1,2-positions (at least), and in consequence reacts somewhat like alizarin, quinalizarin, purpurin and other compounds of this type. Rufigallic acid has not been very extensively studied as an analytical reagent, but de Boer<sup>1</sup> has used it in place of alizarin-sulfonic acid for the detection of zirconium, hafnium and fluoride. For the details of this reaction, refer to the section on alizarinsulfonic acid (page 423). Rufigallic acid has also been considered as a reagent for stannic tin, with which it reacts to give an impure color.<sup>2</sup>

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**2,4,5,7-TETRANITRO-1,8-DIHYDROXYANTHRAQUINONE  
(SODIUM SALT)**

Synonym: 2,4,5,7-tetranitrochrysazin, chrysamin acid

$C_{14}H_4O_{12}N_4$

Mol. Wt. 392.17

Beil. Ref. VIII, 461.



**Use:** Detection of calcium, magnesium and strontium.

The dye is obtained as golden yellow, glistening leaves from water. It is very slightly soluble in boiling water, but its aqueous solution is purple-red in color. It is soluble in alcohol, ether, nitric acid and other mineral acids. It melts with explosion.

**Preparation:** The compound is prepared by warming chrysazin with a large excess of fuming nitric acid on a water bath.<sup>1</sup> Allow to stand for 24 hours. The entire mass eventually crystallizes.

**Detection of calcium, magnesium and strontium.** The sodium salt of tetranitrodihydroxyanthraquinone forms red crystalline precipitates with calcium, strontium, and magnesium salts, and may be used as a sensitive reagent for these metals.<sup>1</sup> Because of the color reaction with calcium and magnesium, Feigl<sup>2</sup> has used this compound to distinguish between distilled water and tap water. This test is more sensitive than that of the similar reaction with hystazarin.

**Reagent.** As reagent, a solution is prepared by adding the solid compound to 100 ml. of N/250 sodium hydroxide. Let the mixture stand, and filter from the undissolved acid. Use the clear filtrate, which contains the sodium salt of the acid. This reagent may be kept in stock.

**Procedure.** Mix one drop of the solution to be tested with one drop of the reagent. With calcium ions, a red crystalline precipitate of the calcium salt forms. This is easily perceptible because of its glistening appearance. The crystals are characteristic under a microscope.

As a drop reaction, 0.0003 mg. in one drop (0.05 ml.) of  $\text{CaCl}_2$  solution can be detected. The limiting concentration is 1:150,000.

Strontium reacts like calcium. Magnesium chloride causes a precipitation in a dilution of 1:1,000.

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## CHAPTER XVI

### MISCELLANEOUS DYES

IN this chapter are grouped a collection of analytically useful dyes, which are not necessarily similar in structure or function. For convenience, these dyes are arranged in alphabetical sequence.

#### ACID ALIZARIN RED G

**Use:** Detection of chromium.

**Preparation:** The dye is prepared by coupling diazotized aminocresol with pyrazolone.

Feigl and Stern<sup>1</sup> have used this dye as a spot test reagent for chromium. The test is similar to that employing acid alizarin yellow RC (below) except that the test paper is prepared in an acid dye bath solution. Chromium causes a spot which, in contrast to the spots formed by other metals, is not affected by hot, dilute sulfuric acid.

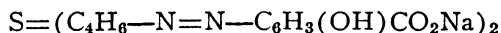
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#### ACID ALIZARIN YELLOW RC

$C_{26}H_{16}N_4O_6SNa_2$

Mol. Wt. 558.45

Color Index, 343.



**Use:** Detection of chromium.

The dye occurs as a brown-yellow paste or powder. It is sparingly soluble in water with a light yellowish-brown color. It also dissolves in concentrated sulfuric acid with a dark reddish-violet solution.

**Preparation:** The dye is prepared by tetrazotizing thioaniline ( $H_2N-C_6H_4-S-C_6H_4-NH_2$ ) and coupling the resulting compound with salicylic acid.

**Detection of chromium.** Acid alizarin yellow RC has been used in a spot test for chromium.<sup>1,3</sup> This is carried out as follows:

**Reagent.** Impregnate filter paper with a boiling ammoniacal solution of the dye and allow to dry.

**Procedure.** Place a drop of the solution to be tested on the dry test paper. Dry and immerse a few seconds in 0.5 N sulfuric acid to destroy the effects of the other elements in the same analytical group of the metals. Rinse with water, and then place the paper in ammonium hydroxide. If chromium is

present, an orange-yellow spot remains on the paper, but if chromium is absent the dye turns orange and dissolves in the ammonium hydroxide. As little as 0.6γ of chromium can be detected by this method.

Gutzeit<sup>2</sup> has used this reagent for the detection of chromium by a contact print method, using gelatin coated paper impregnated with the reagent.

1. F. Feigl and R. Stern, *Z. anal. Chem.* **60**, 1-43 (1921); *C.A.* **15**, 2598 (1921).
2. G. Gutzeit, *Am. Inst. Mining Met. Engs. Tech. Pub. No. 1457*, 13 pp. (1942); *C.A.* **36**, 4047 (1942).
3. F. Feigl, *Mikrochemie*, **1**, 4-20 (1923); *C.A.* **18**, 950 (1924).

## ACID FUCHSIN S(A)

**Use:** Detection of chlorine.

This dye (Color Index, 692) is a mixture of sodium or ammonium salts of the di- and trisulfonates of pararosaniline and rosaniline.

The dye occurs as glistening green metallic granules or as a dark red powder. It dissolves in water with a bluish-red solution, but it is almost insoluble in alcohol. Its sulfuric acid solution is yellow.

**Preparation:** Dry 5 g. of rosaniline at 110° C., and add gradually with stirring to 20 g. of fuming sulfuric acid (20 per cent SO<sub>3</sub>) so that the temperature of the mixture does not fall below 120° C., or rise above 170° C. Dissolve a little of the product in water and test for completeness of sulfonation with a little alkali (no precipitate should form if sulfonation is complete). When sulfonation is complete, mix with water, neutralize with calcium hydroxide, filter, and convert to the sodium salt with sodium carbonate. Evaporate to dryness.

**Detection of chlorine or chlorides.** The color of filter paper that has been impregnated with this dye is changed from red to yellow by exposure to free chlorine.

**Procedure.** Immerse a piece of filter paper in an aqueous solution of the dye and suspend in the mouth of a test tube which contains the sample suspected of containing chloride, a little potassium permanganate, and sulfuric acid. The chlorine formed by the oxidation of the chloride changes the color of the dye from red to yellow.

As little as 0.05 mg. of sodium chloride (0.03 mg. chlorine) responds to this test. Bromine, nitrogen dioxide, hypochlorite, and hypobromite interfere.

1. E. Eegriwe, *Z. anal. Chem.* **74**, 225-31 (1928); *C.A.* **22**, 3859 (1928).

## ANILINE YELLOW S

**Use:** Detection of cobalt, copper, lanthanum, magnesium and nickel.

The dye aniline yellow S, the composition of which is not given by the manufacturers, may be used to detect magnesium, copper, nickel, cobalt, and lan-



thanum. The dye is reported to react like titan yellow, which with magnesium in an alkaline solution yields a red color. Cobalt and nickel compounds give the same reaction. A slightly acid solution (pH 5) of aniline yellow S containing an acetate buffer is yellow-orange in color, but in the presence of a number of metallic ions, a violet color appears. This reaction is particularly sensitive to copper and lanthanum. The following results are reported by Kolthoff:<sup>1</sup>

Blank	Yellow-orange	
Lanthanum	Violet	1 mg. La per liter
Cobalt	Violet	100 mg. Co per liter
Nickel	Violet	100 mg. Ni per liter
Copper	Violet	0.4 mg. Cu per liter

1. I. M. Kolthoff, *Mikrochem., Emich Festschr.* 180-90 (1930); *C.A.* 25, 3267 (1931).

### ANTHRAQUINONE-1-AZO-4-DIMETHYLANILINE

$C_{22}H_{17}O_2N_3$

Mol. Wt. 355.36



**Use:** Detection of lead and tin.

Determination of tin.

Anthraquinone-1-azo-4-dimethylaniline is obtained as dark brown prisms from pyridine. The crystals melt at 249° C. The compound is almost insoluble in alcohol.

**Preparation:** Dissolve 50 g. of 1-aminoanthraquinone in concentrated sulfuric acid, and diazotize with finely divided dry sodium nitrite. Pour the mixture onto ice, and separate the resulting diazo sulfate by filtering with suction. Wash once with ice water. To a clear solution containing 5 g. of the diazo sulfate in water, add a solution of 1.5 g. of dimethylaniline in 10 ml. of alcohol, and allow the mixture to stand with frequent shaking for four hours. Filter off the precipitate which forms, dry on a porous plate, and crystallize from pyridine.<sup>1,2</sup>

**Detection and determination of tin.** The red solution of anthraquinone-1-azo-4-dimethylaniline in alcohol and hydrochloric acid reacts with the stannic ion to form a bluish-violet precipitate, which corresponds in composition to the formula,  $(C_{22}H_{17}O_2N_3)_2H_2SnCl_6$ . This reaction constitutes a very sensitive test for stannic tin.

Filter paper impregnated with the reagent may be used for a spot test by means of which as little as 0.01γ of tin can be detected. The test is most sensitive in solutions saturated with sodium chloride. The limiting dilution of the test is 1:500,000.<sup>3</sup> Somewhat similar reactions are obtained with uranium, molybdenum, gold, zinc, cadmium, mercuric, tetravalent lead, iridium, iron, germanium and aluminum. The tin and uranium spots are the only ones which

disappear when moistened with hydrochloric acid.<sup>4</sup> In dilute solutions of the above ions, however, interference is negligible.

Kuznetsov and Bender<sup>5</sup> have used the above reaction as the basis for a semi-quantitative method for the microchemical determination of small quantities of tin.

**Procedure.** Impregnate filter paper with a warm solution prepared by mixing 0.2 g. of anthraquinone-1-azo-4-dimethylaniline hydrochloride, 4 ml. of hydrochloric acid (d. = 1.12), 30 g. of ammonium chloride, 135 ml. of water, and 60 ml. of alcohol. Dry the paper in air, and store in a container protected from light.

A drop of stannic chloride solution in hydrochloric acid forms a blue-violet spot when placed on the paper prepared as directed above. A visual comparison of the intensity of the color of the spot serves for a semi-quantitative estimation of quantities of tin ranging up to 1γ.

**Detection of lead.** A blue-violet spot is formed when pink reagent paper impregnated with anthraquinone-1-azo-4-dimethylaniline is treated with a drop of a solution containing  $\text{PbCl}_2$ . This reaction may be carried out in the presence of lead chloride and free chlorine.<sup>6</sup>

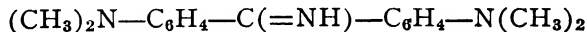
1. A. Schaarschmidt, *Ber.* **49**, 1632 (1916).
2. L. Gattermann and H. Rolfes, *Ann.* **425**, 135-61 (1921).
3. V. I. Kuznetsov, *J. Applied Chem. (U.S.S.R.)*, **13**, 769-75 (1940); *C.A.* **35**, 3190 (1941).
4. V. I. Kuznetsov, *Akad. Nauk. S.S.S.R., Trudy Vsesoyuz Konferentsii Anal. Khim.* **1**, 81-8 (1939); *C.A.* **36**, 1865 (1942).
5. V. I. Kuznetsov and I. M. Bender, *J. Applied Chem. (U.S.S.R.)*, **13**, 1724-31 (1940); *C.A.* **35**, 3922-3 (1941).
6. V. I. Kuznetsov, *J. Applied Chem. (U.S.S.R.)*, **16**, 328-9 (1943); *C.A.* **39**, 472 (1945).

## AURAMIN

Synonym: 4,4'-Bisdimethylaminobenzophenoneimide

$\text{C}_{17}\text{H}_{21}\text{N}_3$

Mol. Wt. 267.34



**Use:** Detection of lead.

Auramin is a solid melting at 136° C. It is insoluble in water, but is slightly soluble in alcohol and ether.

**Preparation:** Heat 12.7 kg. of 4,4'-bisdimethylaminodiphenylmethane with 3.2 kg. of sulfur until the latter is dissolved. Heat to 140° C., and add a mixture of 120 kg. of salt and 7 kg. of powdered ammonium chloride which has previously been heated to 140° C. Raise the temperature to 175° C. and add dry ammonia at about one and one fourth atmospheres pressure for 7 hours. Wash the brownish-yellow product with cold water to remove the salt. Extract the dye with hot water, filter, and precipitate with the salt solution obtained during the previous washing.<sup>1</sup>

**Detection of lead.** Lead salts give a white precipitate with a citric acid solution of auramin. This reaction has been used to detect lead in a solution containing lead, bismuth and copper, which is obtained in the usual scheme of analysis.<sup>2,3</sup>

1. W. Fehrmann, *Ber.* **20**, 2848 (1887).
2. G. Sensi and S. Seghezze, *Ann. chim. appl.* **19**, 392 (1929).
3. G. Sensi and S. Seghezze, *Mikrochemie.* **8**, 210 (1930).

## AZOCARMINE B(B)

**Use:** Detection of chlorine.

Azocarmine B (B) has been used like rosindulin 2B bluish (K) for the detection of chlorides and chlorine. It is a brownish-red powder which dissolves in water with the formation of a bluish-red solution. It is a mixture of phenyl rosinduline and its sulfonate. To make the test, proceed exactly as with rosindulin 2B bluish (K) except that azocarmine B (B) is substituted for the former dye.

1. E. Eegriwe, *Z. anal. Chem.* **74**, 225 (1928).

## AZORUBINE



Mol. Wt. 604.47

Color Index, 184.



**Use:** Detection of nitrate and nitrite.

The compound is a reddish-brown powder. It is soluble in water with a magenta-red solution. It is only slightly soluble in alcohol, but dissolves in sodium hydroxide and sulfuric acid.

**Preparation.** The dye is prepared by coupling diazotized  $\alpha$ -naphthylamine-4-sulfonic acid with  $\beta$ -naphthol-3,6-disulfonic acid.

**Detection of nitrate and nitrite.** The dye azorubine AS assumes a blue or amethyst shade in boiling, concentrated hydrochloric or sulfuric acid; but in the presence of nitric acid or nitrous acid, or the oxides of nitrogen, the dye is converted into pale yellow oxidation products. This reaction has been utilized by Skutil<sup>1</sup> as a sensitive test for nitrite or nitrate.

The test for nitrate and nitrite is carried out as follows:

**Reagent.** Dissolve 0.01 g. of the dye in 100 ml. of water.

**Procedure.** Add 1-3 drops of the azorubine reagent to 1-2 ml. of the solution to be tested, and carefully float the mixture on 1-2 ml. of concentrated sulfuric acid contained in a test tube. As the azorubine diffuses into the acid layer, an amethyst or blue zone appears. In the presence of nitrous or nitric acid, however, a yellow or nearly colorless ring forms between the amethyst zone and the red, overlying solution. If the dye solution, unknown, and sulfuric

acid are mixed by shaking, the dye is decomposed and a yellow or colorless solution remains.

The presence of chloride ions increases the sensitivity of the reaction. Sodium nitrate at a dilution of 1:800,000 may be detected by the above procedure.

Azorubine is not specific for nitrate and nitrite, since it reacts with chlorate, iodate, selenic and selenious acids, telluric acid, ferricyanide, hydrogen peroxide, manganate, chromate, bromate, and vanadate. It does not, however, react with iron salts, fuming sulfuric acid, and ferrocyanide, and in this important respect differs from diphenylamine. In testing water, the presence of urine, iron, soils, and organic matter apparently does not affect the reaction. For this reason azorubine is superior to diphenylamine for the detection of nitrite and nitrate, since it can be used in solutions containing iron and soil extracts.

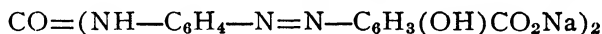
1. F. Skutil, *Chem. Listy*, **30**, 74-7 (1936); *C.A.* **30**, 7059 (1936).

### BENZO FAST YELLOW 5GL

$C_{27}H_{18}N_6O_7Na_2$

Mol. Wt. 584.41

Color Index, 346.



**Use:** Detection of chromium, copper, iron and nickel.

The dye is a greenish-yellow powder. It is sparingly soluble in hot water giving a yellow color to the solution. It is insoluble in alcohol, but dissolves in sodium hydroxide with an orange color, and in sulfuric acid with an orange-red solution.

**Preparation:** Dissolve 5 g. of acetyl-*p*-phenylenediamine in 15 g. of 32 per cent hydrochloric acid, 66 ml. of water, and 67 g. of ice, and then diazotize with a solution containing 2.35 g. sodium nitrite dissolved in 7 ml. of water. Add the resulting mixture to a solution of 5 g. salicylic acid and 15 g. of sodium carbonate in 100 ml. of water and 50 g. of ice. Allow to stand 24 hours and filter. Add to 100 g. concentrated sulfuric acid, and heat on a water-bath 4 hours. Dilute with water, filter, stir the brown precipitate with 250 ml. of water and 150 g. of ice, and then neutralize by the careful addition of a sodium carbonate solution. Pass phosgene into this solution with constant stirring until the mixture is acid. Filter and neutralize with sodium carbonate.<sup>2</sup>

**Detection of copper, iron, chromium and nickel.** Stearns<sup>1</sup> has recently studied the sensitivity of the reaction between copper and benzo fast yellow 5GL, and has found that by means of spectrophotometric measurements extremely small quantities of the metal can be detected. Iron, chromium, and nickel also give sensitive color reactions with the dye, but the optimum analytical conditions for these reactions have not been determined.

By means of a spectrophotometric measurement, about 0.0001 mg. of copper per liter can be detected. Employing a similar technique, only 0.004 mg. of copper per liter can be detected by means of the color reaction with sodium diethyldithiocarbamate; hence, by means of spectrophotometric measurements, the benzo fast yellow 5GL test is about 40 times as sensitive as that with sodium

diethylthiocarbamate. The carbamate test, based on visual colorimetry, has a sensitivity of about 0.01 mg. of copper per liter, and this is not greatly different from the spectrophotometric sensitivity; but visually the sensitivity of the yellow dye is considerably lower than the spectrophotometric sensitivity because the change of color (yellow or reddish-yellow) is not so pronounced as the color change in the copper-carbamate reaction. Consequently, there is little difference in the sensitivity of the two methods when visual colorimetry is employed, but the benzo fast yellow 5GL is far superior with the spectrophotometer.

The sensitivity of the dye toward iron is only about 0.05 mg. of copper per liter, and is probably similar for chromium and nickel.

The reaction between the dye and such metals as copper, iron, chromium, and nickel has been used to determine the purity of distilled water.

1. E. I. Stearns, *Ind. Eng. Chem., Anal. Ed.* **14**, 568-9 (1942); *C.A.* **36**, 4773 (1942).
2. C. Bülow, *Ber.* **44**, 605 (1911).

### BROMPHENOL BLUE

Synonym: Tetrabromphenolsulfonphthalein

$C_{19}H_{10}O_5Br_4S$

Mol. Wt. 670.01

Beil. Ref. XIX (649).

**Use:** Detection of lead and mercury.

Bromphenol blue is a pale orange-colored crystalline powder. It is slightly soluble in water and in ether, but is soluble in alcohol or dilute alkali hydroxide solutions. Its aqueous solution is yellow at pH 3, but is purple at pH 4.6.

**Preparation:** Suspend 5 g. of phenolsulphonphthalein in 40 ml. of glacial acetic acid and heat to boiling, and then add gradually a solution of 5 ml. of bromine in 20 ml. of glacial acetic acid, while keeping the original mixture just below the boiling point. When all phenolsulfonphthalein is dissolved, and the yellow solid has settled, filter, wash free of bromine with acetic acid, and dry in air. The product may be purified by recrystallization from boiling glacial acetic acid or from a mixture of acetone and acetic acid.<sup>1</sup>

**Detection of mercury and lead.** Kocsis<sup>2</sup> has used bromphenol blue as a reagent for the detection of mercury and lead by means of a spot test. As little as 0.02 mg. of mercuric ion yields a yellow spot with bromphenol blue. A violet-red ring is obtained with as little as 0.025 mg. of lead.

1. E. C. White and S. F. Acree, *J. Am. Chem. Soc.* **41**, 1205 (1919).
2. E. A. Kocsis, *Mikrochemie.* **27**, 180-4 (1939); *C.A.* **34**, 51 (1940).

### CERULEIN (By)

$C_{20}H_{10}O_6$

Mol. Wt. 346.28

Color Index, 783.

**Use:** Detection of molybdenum, tin, titanium, tungsten, uranium and vanadium.

The dye occurs as a black powder or paste. It is insoluble in alcohol and water, but the addition product with sodium bisulfite is soluble. Many of the soluble forms of the dye are in reality bisulfite addition compounds.

**Preparation:** Heat 10 g. of dry gallein with 200 g. of concentrated sulfuric acid at 190-200° C. with agitation until a sample no longer gives the red color of gallein with alcohol. Cool, and pour the mixture into 100 ml. of water, and then filter and wash the precipitate. Dissolve the residue in sodium carbonate and filter, and then salt out the dye from the hot filtrate, and finally filter hot. Wash the residue with a 10 per cent sodium chloride solution until the filtrate is colorless, and then decompose with hydrochloric acid.

**Fluorescence analysis.** A number of ions may be detected by the fluorescence which they produce with cerulein:<sup>2</sup>

(a) *Tin*: Stannous tin reacts with cerulein to give a yellowish-green fluorescence. Only 0.02γ of tin gives the test.<sup>1</sup> In certain qualitative schemes, stannic tin is reduced with iron, but the presence of the ferrous iron which is formed interferes with most color reactions which might otherwise be used to detect stannous tin. Cerulein is particularly useful for tin detection under such circumstances, since it can be used in the presence of ferrous ions.<sup>3</sup>

(b) *Molybdenum*: An acid solution of molybdenum which has been reduced with zinc gives a yellow fluorescence with an ethyl alcohol suspension of the dye when only 0.025γ of molybdenum is present.<sup>1</sup>

(c) *Vanadium*: An acid solution of vanadium which has been reduced with zinc gives a fluorescence reaction with cerulein when only 0.5γ of vanadium is present.<sup>4</sup>

(d) *Uranium, Titanium, and Tungsten*: Uranyl, titanium, and tungsten compounds react with cerulein in much the same manner as vanadium and molybdenum.<sup>4</sup>

1. H. Gotō, *Science Rpts. Tohoku Imp. Univ. First Ser.* **29**, 204-18 (1940); *C.A.* **35**, 1720-3 (1941).
2. H. Gotō, *J. Chem. Soc. Japan.* **59**, 547-54 (1938); *C.A.* **32**, 5721 (1938).
3. E. Eegriwe, *Z. anal. Chem.* **74**, 225-31 (1928); *C.A.* **22**, 3859 (1928).
4. H. Gotō, *Science Rpts. Tohoku Imp. Univ. First Ser.* **29**, 287-303 (1940); *C.A.* **35**, 1720-3 (1941).

## 5-CHLORO-1-AMINO-4-BROMO-2-ANTHRAQUINONESULFONIC ACID

Synonym: 5-Chlorobromamine acid

$C_{14}H_7O_6NSBrCl$

Mol. Wt. 416.64



**Use:** Detection of zirconium.

**Detection of zirconium.** Bromamine acid is the name applied to the sodium salt of 1-amino-4-bromo-2-anthraquinonesulfonic acid. A number of substituted bromamine acids have been found to react with tri- and tetravalent cations to form red precipitates. In acid solutions the activity of these compounds is restricted to only a few ions, of which the reaction with zirconium is the most sensitive. The 5-chloro derivative has been recommended by Yoe

and Overholser<sup>1</sup> as the most satisfactory reagent for the detection of zirconium. In addition to zirconium, chlorobromamine acid yields heavy bright red precipitates with cadmium, copper, cobalt, nickel, palladium and zinc in ammoniacal solutions.

The following procedure is used for the detection of zirconium:

**Reagent.** Dissolve 0.2 g. of the dye in 100 ml. of a 50 per cent acetone-water solution.

**Procedure.** Place 0.05 ml. of the solution to be tested on a white spot plate, and add 0.05 ml. of nitric acid and 0.03 ml. of the 5-chlorobromamine acid solution. Shake the spot plate for several minutes to increase the reaction rate, and observe the color which appears. With zirconium a red color is formed. The test may be made more sensitive by preparing a blank in a similar manner, except that distilled water is used instead of the test solution. In some instances a pale red-colored precipitate may float on the surface of the blank, but this should not be confused with the precipitate which is formed in the presence of zirconium. The latter is more granular and is darker colored, and settles to the bottom of the reaction mixture.

The smallest quantity of zirconium which can be detected in the absence of interfering ions is about 2 p.p.m. About 5 minutes of continuous shaking is required for development of the color at this dilution, and a blank must be used for comparison. The reaction rate is very slow at 5 p.p.m., and the test is not entirely satisfactory with quantities of zirconium below 10 p.p.m.

Phosphate and sulfate prevent the formation of a precipitate with zirconium, and fluoride must be absent. A number of cations interfere if present in relatively high concentration. Tetravalent cerium, beryllium, aluminum, chromium, thorium, and titanium are particularly objectionable.

1. J. H. Yoe and L. G. Overholser, *Ind. Eng. Chem., Anal. Ed.* 15, 73 (1943); *C.A.* 37, 1671 (1943).

## CHROME RED ACIDOL

**Use:** Detection of chromate.

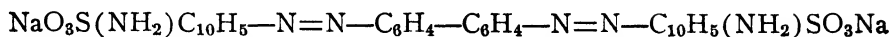
**Detection of chromate.** Chrome Red Acidol is an azo dye that has been used by Gutzeit<sup>1</sup> for the detection of chromates. The procedure is as follows:

**Procedure.** Place 2-3 drops of the solution to be tested on a watch glass and make alkaline with sodium hydroxide. Heat to boiling and add a few drops of hydrogen peroxide or sodium peroxide. Shake and filter, and then place 3 drops of the filtrate on a piece of filter paper. Acidify by treating the spot with concentrated hydrochloric acid, and treat the spot with a solution of chrome red acidol and dry. A red spot indicates the presence of chromium.

1. G. Gutzeit, *Helv. Chim. Acta.* 12, 829-50 (1929).

**CONGO RED**

$C_{32}H_{22}N_6O_6S_2Na_2$  Mol. Wt. 696.66 Beil. Ref. XVI, 410. Color Index, 370.



**Use:** Detection of boric acid, cyanide and hydrochloric acid.

Determination of hydrochloric acid, iron and titanium.

Congo red is a brownish-red powder. It is soluble in 10 parts of cold water, but is more soluble in hot water. It is soluble in alcohol, but insoluble in ether.

**Preparation:** Dissolve 48.4 g. of benzidine in 300 ml. of water containing 20 ml. of concentrated hydrochloric acid, using heat if necessary. Add ice until the temperature falls to below 5° C. Add 30 ml. of concentrated hydrochloric acid, and then add about 14.4 g. of sodium nitrite in a 10 per cent aqueous solution until diazotization is complete. Dissolve 150 g. of sodium naphthionate in the least possible quantity of water, and into this solution allow the diazo solution to run slowly with stirring. Allow to stand 30 minutes, and add gradually 35 g. of sodium carbonate so that during further stirring the solution is always alkaline. Heat slowly to about 80° C., and saturate the solution with salt. Cool, filter, and wash the dye with a saturated salt solution and dry.

**Detection and determination of hydrogen cyanide.** The most suitable tests for hydrogen cyanide for industrial use appear to be those using Congo red and silver nitrate, and benzidine and copper acetate. Both of the reactions may be made quantitative. The Prussian blue and thiocyanate tests are specific but not delicate, and the picrate test is neither specific nor delicate.<sup>1</sup>

**Reagent.** Immerse a strip of filter paper for one minute in a 0.05 per cent solution of Congo red, and then one minute in a 5 per cent solution of silver nitrate. Dry as quickly as possible, and cut one inch from each end of the strip of paper and discard these pieces.

**Procedure.** The air to be tested is drawn through the test paper with the aid of a pump, and from the depth of the stain produced, the concentration of hydrogen cyanide in air is obtained by reference to a standard color chart.

The sensitivity of this reaction is diminished by the presence of any alkaline or acid gas, but these gases may be removed by first passing the air through Congo red paper containing no silver nitrate before making the test.

**Detection of boric acid.** The following test may be used for the detection of boric acid:

**Procedure.** Add one drop of boric acid solution to one drop of a 0.1 per cent solution of Congo red and evaporate to dryness on a water-bath. The blue residue dissolves in water, alcohol, methyl alcohol, or acetone to yield a red solution. This color change may be obtained with 0.1 ml. of 0.01 per cent boric acid.



A less sensitive test may be performed by adding a 4 per cent solution of boric acid to Congo red paper. The color is unchanged at first, but when the paper is heated cautiously over a small flame a blue color appears. The red color reappears when the dried paper is exposed to moist air.

Boric acid is the only acid giving this color change, but certain zinc, aluminum, manganese, magnesium, ammonium, nickel, cobalt, and ferrous salts cause the same effect and must be absent while making the test. Boric acid may be removed by converting to the volatile methyl ester.

The blue color is due to the formation of metaboric acid. On heating to a higher temperature, pyroboric acid is formed and the red color restored.<sup>2</sup>

**Determination of titanium and iron.** Color filters, which may be used instead of color standards for the colorimetric determination of titanium and iron, may be prepared by coating glass with gelatin colored with Congo red and picric acid.<sup>3</sup>

1. Anon., *Dept. Sci. Ind.-Research (Brit.)*, *Methods for Detection of Toxic Gases in Industry*, Leaflet No. 2, 9 pp. (1938); *C.A.* 32, 8302 (1938).
2. J. Stamm, *Pharmacia*. (1924).
3. F. Ya. Galakhov, *Zavodskaya Lab.* 10, 90-2 (1941); *C.A.* 35, 5055 (1941).

### ***o*-CRESOLPHTHALEIN**

$C_{22}H_{18}O_4$

Mol. Wt. 346.36    Beil. Ref. XVIII, 153 (381).

**Use:** Determination of hydrogen cyanide.

*o*-Cresolphthalein is a reddish-yellow crystalline powder. It is slightly soluble in water but is soluble in alcohols.

**Determination of hydrogen cyanide.** Nicholson<sup>1</sup> recommends the use of *o*-cresolphthalein in place of phenolphthalein for the determination of hydrogen cyanide. The method depends on the oxidation in a basic solution of reduced *o*-cresolphthalein (*o*-cresolphthalin) to the colored phthalein by hydrogen cyanide in the presence of copper. The resulting color is measured in a colorimeter. This reaction is said to be sensitive to 1 part of cyanide in 100,000,000.

*o*-Cresolphthalin may be prepared as follows:

**Preparation:** Mix 300 mg. of *o*-cresolphthalein with 15-20 ml. of water and 5 ml. of 50 per cent sodium hydroxide, and reduce by heating under reflux with the addition of small quantities of zinc dust. Continue to heat the mixture for some time after complete decolorization, and then cool, dilute, and filter through a sintered glass filter. Make the filtrate strongly acid with concentrated hydrochloric acid with cooling. Filter off the precipitate and wash thoroughly with dilute hydrochloric acid, and then dry in an oven.

Cyanide is determined by the following procedure:

**Reagents.** *o*-Cresolphthalin reagent: Dissolve 40 mg. of *o*-cresolphthalin in 10 ml. of alcohol and dilute to 20 ml. with water. This solution gradually oxidizes and should be freshly prepared.

**Copper reagent:** Dissolve 150 mg. of copper sulfate,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , in 100 ml. of water.

**Sodium sulfite reagent:** Prepare triethanolamine hydrochloride by passing hydrogen chloride gas into an alcoholic solution of the base and recrystallize from alcohol. Then dissolve 5 g. of anhydrous sodium sulfite and 0.224 g. of triethanolamine hydrochloride in 100 ml. of water.

**Copper sulfate-triethanolamine hydrochloride solution:** Dissolve 300 mg. of copper sulfate and 0.896 g. of triethanolamine hydrochloride in 100 ml. of water.

**Cresol red reagent:** Dissolve 50 mg. of cresol red in 125 ml. of alcohol and dilute with water to 250 ml. To 5 ml. of this solution, add 2 ml. of 0.5 N sodium hydroxide solution and 2 ml. of the copper sulfate-triethanolamine hydrochloride solution and dilute to 200 ml. This solution should be prepared from the phenol red mixture every two days.

**Procedure.** Treat the solution containing 0.01-0.1 mg. of hydrogen cyanide in a 50-ml. graduated flask with 0.5 N sodium hydroxide so that 1.5 ml. of 0.5 N sodium hydroxide is finally present. Adjust the volume to 45 ml. and cool. Note the temperature, and add 1 ml. of the *o*-cresolphthalin solution and mix. Then quickly add 1 ml. of the copper reagent, stopper the flask and shake well. After exactly 5 minutes as measured by a stop watch, add 2 ml. of the sodium sulfite reagent to halt further action. Mix immediately, dilute to 50 ml., and transfer to a colorimeter. After 5 minutes (10 minutes after the beginning of the reaction) read the colorimeter. Make a calibration curve with alkaline mixtures of cresol red and copper sulfate and triethanolamine hydrochloride, which is maintained at the same dilution. The determination should be carried out at a temperature of within  $1^\circ \text{C}$ . of that at which the curve is determined.

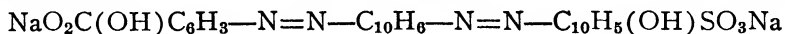
1. R. I. Nicholson, *Analyst*. **66**, 189-92 (1941); *C.A.* **35**, 5063 (1941).

## DIAMOND BLACK F

$\text{C}_{27}\text{H}_{16}\text{N}_4\text{O}_7\text{SNa}_2$

Mol. Wt. 586.46

Color Index, 299.



**Use:** Detection and determination of beryllium, cadmium, calcium, cobalt, copper, magnesium, nickel, strontium, uranium and zinc.

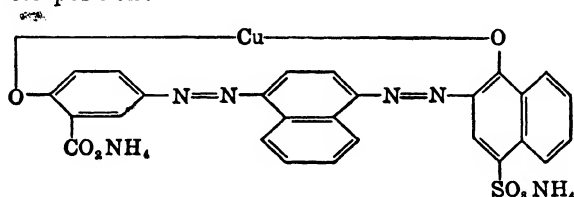
Diamond black F is a brownish-black powder which dissolves in water to form a bluish-violet solution.

**Preparation:** Diazotize *p*-aminosalicylic acid and add a quantity of the resulting insoluble diazo compound corresponding to 5 g. of sodium nitrite to a solution of 10 g. of  $\alpha$ -naphthylamine in hydrochloric acid. Add sodium acetate to precipitate the steel-blue product and allow the mixture to stand for 24 hours. Warm to  $50^\circ \text{C}$ ., acidify with hydrochloric acid and filter. Dissolve the precipitate in hot water with the addition of sodium hydroxide, cool, and add 5 g. of sodium nitrite. Allow the mixture to stand for 3-4 hours, acidify, and

filter off the resulting diazo compound. Add this to an alkaline solution containing 20 g. of  $\alpha$ -naphthol-4-sulfonic acid and salt out the resulting dye.

**Reactions with the metals.** A number of metals, including copper, beryllium, magnesium, zinc, cadmium, calcium, strontium, uranium, iron, nickel and cobalt, may be detected by the color reaction which is obtained when an ammoniacal solution of the dye is added to a solution of the metal that has been made alkaline with ammonium hydroxide. A red color is obtained with copper, magnesium, zinc, calcium and iron.<sup>1</sup>

The above metals can be determined by a microtitration process based upon titration with a standard solution of the dye. With copper, for example, one mole of the dye reacts with 1 mole of copper to form an inner-complex having the following composition:



By adding a standard solution of the dye to a solution of copper ion, the latter can be determined. Since an ammoniacal solution of a copper salt is blue, and the copper reacts with the reagent to form a red complex, the end-point of the titration is attained when upon the addition of a drop of the dye solution the blue color changes to red. The standard solution of the dye is prepared as follows:

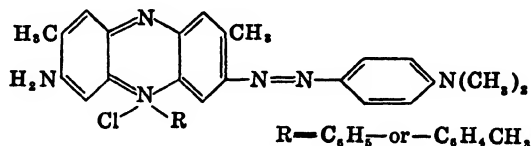
**Procedure.** Add 0.092 g. of the dye and about 1 ml. of 2 N sodium carbonate solution to distilled water and dilute to 1 liter. Standardize against a solution containing a known quantity of copper. This reagent is suitable for titrating 1 ml. of a solution containing 0.01 mg. of copper.

1. C. Brenner, *Helv. Chim. Acta.* 3, 97-103 (1920).

## DIAZINE GREEN S(K)

Synonym: Janus green

Color Index, 133.



**Use:** Detection of tin.

This compound occurs as a dark green or brown powder.

**Preparation:** Dazine green S(K) is prepared by diazotizing safranine and coupling the resulting diazo compound with dimethylaniline.

**Detection of tin.** Diazine green S(K) dissolves in hydrochloric acid with the formation of a blue solution, but in the presence of a trace of stannous tin, a violet shade appears, and this finally passes into a red safranin color.<sup>1</sup>

**Procedure.** Dissolve the precipitate of  $\text{Sb}_2\text{S}_3$  and  $\text{SnS}_2$  obtained in the usual analytical procedure in the smallest possible volume of concentrated hydrochloric acid. Reduce with iron and add 5 ml. of 0.01 per cent aqueous solution of the dye which has been turned clear blue by the addition of hydrochloric acid. One drop of solution containing 0.002 mg. tin gives the color reaction within 5 minutes.

Ferrous salts and other common reducing agents exert little influence on this reagent.

1. E. Eegriwe, *Z. anal. Chem.* **74**, 225-31 (1928) ; *C.A.* **22**, 3859 (1928).

### DI-[9,10-MONOHYDROXYPHENANTHRYL] AMINE

 $\text{C}_{28}\text{H}_{19}\text{O}_2\text{N}$ 

Mol. Wt. 401.43

Beil. Ref. XIII, 725.



**Use:** Detection of nitrate and nitric acid.

This compound occurs as a brown powder. It melts at 230° C. with decomposition. It is insoluble in most solvents, but dissolves in concentrated sulfuric acid with the formation of a blue color.

**Preparation:** Heat 5 g. of 9,10-dihydroxyphenanthrene with 250 ml. of concentrated ammonium hydroxide on a water-bath. When ammonium hydroxide is poured over the reaction product, which has been cooled to room temperature, a clear red-brown solution is formed. In a short time, however, a yellowish-green flocculent precipitate appears. Allow the mixture to stand 9-10 hours with heating, and replace the ammonia which is expelled during the treatment. Filter, and heat the brown product with alcohol to dissolve any unchanged dihydroxyphenanthrene.<sup>1</sup>

**Detection of nitric acid and nitrates.** A solution prepared by dissolving 0.1 g. of pure di-[9,10-monohydroxyphenanthryl]amine in a liter of concentrated sulfuric acid is deep blue in color, and in the presence of nitric acid or nitrates this color turns to a wine-red. When a small particle of the solid to be tested is added to 2-3 ml. of the reagent, the color change occurs immediately. The presence of water diminishes the sensitivity of the reaction, but chlorate and chromate do not interfere seriously. Large quantities of nitrite cause the same color change as does nitric acid, probably due to the oxidation of nitrite to nitrate.<sup>2</sup>

1. J. Schmidt and H. Lumpp, *Ber.* **43**, 790 (1910).
2. J. Schmidt and H. Lumpp, *Ber.* **43**, 794-7 (1910) ; *C.A.* **4**, 1725 (1910).

**EOSIN**

Synonym: Tetrabromofluorescein



Mol. Wt. 647.93

Beil. Ref. XIX, 228.

**Use:** Detection of fluoride.

The sodium salt of eosin consists of reddish crystals having a bluish tinge, or occurs as a brownish-red powder. It is freely soluble in water but is less soluble in alcohol, and is insoluble in ether. A concentrated aqueous solution of the dye is deep brownish-red in color, but the dilute solution is yellowish-red with a greenish fluorescence. The alcoholic solution exhibits a strong green fluorescence.

**Preparation:** Place 16.5 g. of fluorescein and 80 ml. of alcohol in a flask, and add dropwise 12 ml. of bromine from a separatory funnel during the course of approximately 20 minutes. Allow the mixture to stand for two hours, and filter off the precipitate. Wash several times with alcohol, and dry over a water-bath. Finally remove the alcohol of crystallization by drying at 110° C. To convert to the sodium salt, grind 6 g. of eosin with 1 g. of anhydrous sodium carbonate. Transfer the mixture to a wide-necked Erlenmeyer flask, moisten with a little alcohol, and add 5 ml. of water. Warm on a water-bath until carbon dioxide is no longer evolved, and then add 20 g. of alcohol. Heat to boiling and filter the hot solution. The crystals of the sodium salt separate from the filtrate on cooling. Filter with suction and wash with alcohol.<sup>1</sup>

**Detection and determination of fluorides.** Meyer and Schulz<sup>2</sup> have proposed a procedure for determining fluorides based upon the precipitation of lanthanum fluoride, but this method generally has proved unsatisfactory because of the difficulty in obtaining pure, filterable  $\text{LaF}_3 \cdot 3\text{H}_2\text{O}$  precipitates. The marked tendency of lanthanum fluoride to adsorb other ions, however, can be utilized in making the qualitative test for fluorides more sensitive. By using a suitable dye, a colored precipitate of lanthanum fluoride is obtained instead of the colorless crystalline compound. In this way traces of fluorides can be detected, whereas without the use of the dye the colorless precipitate might pass unobserved. Eosin has proved the most satisfactory dye for this purpose.<sup>3</sup>

**Procedure.** To 1 ml. of the acetic acid solution to be tested add 0.5 ml. of a saturated sodium acetate solution, 1 drop of 0.2 per cent eosin solution and 0.5 ml. of 1 per cent lanthanum acetate solution in very dilute acetic acid. Boil for a short time, cool, and centrifuge. If fluoride is present, a red precipitate is formed.

With slight modification this test can be used to test as little as 0.002 mg. of fluoride in 3 drops of solution. The presence of phosphate, oxalate, molybdate, and large concentrations of alkali salts interfere with this test.

1. A. Bayer, *Ann.* **183**, 1 (1876).
2. R. J. Meyer and W. Schulz, *Z. angew. Chem.* **38**, 203-6 (1925).
3. J. Fischer, *Z. anal. Chem.* **104**, 344-6 (1936); *C.A.* **30**, 4431 (1936).

**EUCHRYSIN-3R** $C_{17}H_{20}N_3Cl \cdot ZnCl_2$ 

Mol. Wt. 438.09

Color Index, 788.

**Use:** Detection of oxygen.

Euchrysin-3R is a orange powder which dissolves in water to form an orange-yellow solution with a greenish fluorescence. The alcoholic solution is also orange-yellow and exhibits a greenish fluorescence.

**Preparation:** Dissolve 14 kg. of *m*-aminodimethylaniline in 30 liters of alcohol and 5 liters of concentrated hydrochloric acid. Then add 3.5 liters of 40 per cent formaldehyde to the cold solution. Isolate the tetramethyltetraminodiphenylmethane by the addition of an alcoholic solution containing 6 kg. of sodium acetate. Heat the product to 140° C. with dilute hydrochloric acid and oxidize with ferric chloride.

The following method may be used:

Dissolve 2.5 kg. of the tetramethyltetraminodiphenylmethane in 35 kg. of concentrated sulfuric acid and to the cold solution add 2 kg. of nitric acid ( $d = 1.38$ ), diluted with sulfuric acid. Allow to stand for some time and pour the mixture into 250 liters of cold water and reduce with 8 kg. of zinc dust with stirring. Filter, concentrate by evaporation and heat to 140° C. for some time. Oxidize with air, cool, dissolve in water, and salt out.

**Detection of oxygen:** Traces of oxygen can be detected by the destruction of the fluorescence of euchrysin-3R. By this method oxygen at pressures as low as 0.0005 mm. of mercury can be detected. The dye is adsorbed by well-aged gels of the highly polymerized inorganic acids or hydroxides such as silica or aluminum hydroxide. The adsorbent must be neither opaque nor colored.<sup>1</sup>

1. H. Kautsky and A. Hirsch, *Z. anorg. allgem. Chem.* **222**, 126-34 (1935); *C.A.* **29**, 4288 (1935).

**FAST BLUE R**

Synonym: Meldola's Blue

 $C_{18}H_{15}N_2OCl$ 

Mol. Wt. 310.76

Color Index, 909.

**Use:** Detection of sulfite.

Fast blue R is a dark violet powder which possesses a bronze luster. It dissolves in water with the formation of a bluish-violet solution. It also dissolves in alcohol with the formation of a blue solution.

**Preparation:** Fast blue R is prepared by the action of nitrosodimethylaniline on  $\beta$ -naphthol in a hot alcoholic solution.

**Detection of sulfites:** Eegriwe<sup>1</sup> has used the oxazine dye, fast blue R, also referred to in *Chemical Abstracts* as "true blue R" for the detection of sulfites. The reaction is based upon the reducing properties of the sulfite ion. Thionates and thiosulfates do not give this reaction.

To make the test proceed as follows:

**Procedure.** Remove sulfides, polysulfides and hydroxides by adding a suspension of cadmium carbonate, and then introduce carbon dioxide until phenolphthalein no longer reddens the solution. Then add dropwise a 0.01 per cent solution of fast blue R, shaking after each drop has been added, until the violet color disappears. If 0.01 mg. of  $\text{SO}_2$  is present in 1 ml. of solution, it will decolorize 8 drops of the reagent. As little as 0.002 mg. of sulfur dioxide gives a satisfactory test (formation of a yellow color).

1. E. Eegriwe, *Z. anal. Chem.* **69**, 382-5 (1926); *C.A.* **21**, 873 (1927).

## FLUORESCCEIN

Synonym: Dihydroxyfluorane, resorcinolphthalein

$\text{C}_{20}\text{H}_{12}\text{O}_5$

Mol. Wt. 332.30

Beil. Ref. XIX, 222.

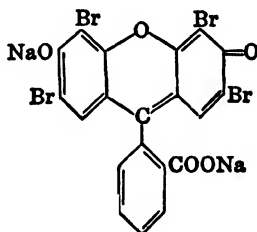
**Use:** Detection of arsenate, boric acid, bromate, bromide, cyanide, hydrogen peroxide, lead, mercury, oxygen, ozone and silver.

Determination of arsenate, bromide, cyanide, and ozone.

Fluorescein is a yellowish-red to red powder. It melts in a sealed tube at  $314\text{--}316^\circ\text{C}$ . with decomposition. It is insoluble in water, benzene, chloroform and ether, but dissolves in hot alcohol or glacial acetic acid. It also dissolves in alkali hydroxides or carbonates with a bright green fluorescence. The solution appears red by transmitted light.

**Preparation:** Grind 15 g. of phthalic anhydride with 22 g. of resorcinol in a mortar, and heat the mixture in an oil-bath to  $180^\circ\text{C}$ . Add slowly over a period of about 10 minutes 7 g. of zinc chloride, which has previously been dehydrated by fusing and then powdered. Then raise the temperature to  $210^\circ\text{C}$ . and continue heating until the mass has completely solidified. This usually requires from 1 to 2 hours. Allow the melt to cool. Break up the mass, transfer to a porcelain vessel containing 200 ml. of water and 10 ml. of concentrated hydrochloric acid, and boil for 10 minutes. Separate the fluorescein from the aqueous liquid by filtration, and wash the precipitate with water until the filtrate is no longer acid. Dry the fluorescein on a water-bath. The raw material may be purified by dissolving in sodium hydroxide solution and re-precipitating with hydrochloric acid.<sup>1</sup>

**Detection of bromine and bromides.** The yellow dye fluorescein is converted into the red tetrabromo derivative, eosin,



by the action of free bromine. The color change which occurs makes this reaction suitable for the detection of small quantities of bromine. Since bromides are easily converted to free bromine with various oxidizing agents, the reaction can also be used as a sensitive test for bromides. The use of the bromination of fluorescein as a means for detecting small quantities of bromine appears first to have been suggested by Baubigny,<sup>2-6</sup> and has since been extensively studied by many investigators.<sup>7-11,42</sup> The test may be carried out either by the action of bromine on a fluorescein solution or upon filter paper which has been impregnated with the reagent. The following method is based upon Baubigny's procedure as modified by Ganassini:<sup>8</sup>

**Reagent.** Impregnate a strip of filter paper with a saturated solution of fluorescein in a 1:1 alcohol-water mixture. For the detection of traces of bromine, the dye should be recrystallized twice from 80 per cent alcohol.

**Procedure.** Place a drop of the solution to be tested, along with a few particles of lead peroxide and a few drops of acetic acid, in a small test tube, and cover with a strip of filter paper impregnated with fluorescein as described above. Warm gently and observe the reagent paper for the appearance of a red spot. With a suitably designed apparatus as little as 2 $\gamma$  of bromine can be detected at a concentration of 1:25,000. Chromic acid may be substituted for lead peroxide.

Chlorides do not affect the above reaction, since they are practically unchanged by treatment with lead peroxide and acetic acid. Thus it is possible to carry out the test for bromine in the presence of large quantities of chloride. Free chlorine, if any is formed, yields a white coloration with fluorescein and consequently does not interfere generally with the bromine test. Iodides, however, are oxidized to free iodine under the conditions of the above procedure, and also from a colored iodo derivative with fluorescein. Iodides may be removed from the reaction mixture by treatment with nitrous acid or ferric salts,<sup>9,10</sup> or by oxidizing to iodate by warming the solution to be tested with potassium permanganate.

According to Murmann<sup>12</sup> the test may not be successful when nitrous or nitric acid is present, but this difficulty can be overcome by reduction with zinc. The following procedure has been described by Lorentz<sup>13</sup> and co-workers.

**Reagent.** Treat a little finely ground fluorescein with a mixture of 35 parts of acetic acid and 65 parts of water and stir for about 1 hour. Filter, and moisten strips of S & S filter paper No. 604K, or bleached silk with this solution and dry in air. Store in the dark.

**Procedure.** Place the solution to be tested in a small (approximately 50-ml.) flask which has a straight cylindrical neck and is provided with a glass cap which is not quite air tight. Place a square of the reagent paper, which is about 0.5 cm. to the side, in the glass cap and moisten with a drop of water. Fill the flask almost up to the neck with the solution, and then add 5 ml. of a concentrated potassium permanganate solution and 0.02 ml. of concentrated sulfuric acid. Place the cap, containing the reagent paper, over the mouth of



the flask and allow the mixture to stand for about 15 minutes, avoiding direct exposure to sunlight. In this way about 0.01 mg. of potassium bromide can be detected in 50 ml. of solution.

By comparing the depth of the red color obtained in this test with that produced with known quantities of bromide, it is possible to make a fairly accurate estimation of the quantity of bromide present.

Baines<sup>14</sup> has used the following modification of the fluorescein-bromine reaction.

**Reagents.** *Sodium fluoresceinate solution:* Mix 30 ml. of 10 per cent sodium hydroxide, 20 ml. of glacial acetic acid and 1 ml. of a 0.25 per cent solution of sodium fluoresceinate and 49 ml. of water.

*Chlorine solution:* An approximately 0.0001 N solution of chlorine or of sodium hypochlorite.

**Procedure.** Add 5 or 6 drops of the sodium fluoresceinate solution to 1 ml. of the solution to be tested, and then add the chlorine solution dropwise with shaking after each addition. If bromide is present, a pink coloration is obtained. This is bleached by the further addition of chlorine. This reaction is very delicate.

This test cannot be used in the presence of reducing agents other than bromides, nor can it be used when the solution is colored. In the absence of bromide, the above test can be used for the detection of iodides, since the iodo- and bromo-derivatives of fluorescein are similar in color, although their absorption spectra are very different.

Aickin<sup>15</sup> has used the fluorescein reaction for the detection of bromides in the presence of large quantities of chloride. His test was specifically applied to the detection of bromides in pure cupric chloride. Belote<sup>16</sup> has used a similar procedure for the detection of bromides in body fluids.

Pavlinova<sup>17</sup> has detected bromides by the fluorescein reaction, but has used pernitric acid, which is formed by the interaction of hydrogen peroxide and nitrous acid, to liberate bromine from bromides.

**Procedure.** Place a drop of an alkaline solution of fluorescein on a strip of filter paper and allow to dry. Place a drop of 5-10 per cent sodium nitrite solution and 3 per cent hydrogen peroxide and 1 drop of dilute sulfuric acid near this drop, and at the point of contact of the two, place a drop of the solution to be tested. A red spot is formed if bromide is present. In the presence of small quantities of bromide, a red color appears only after holding over a bottle of ammonia. In the presence of iodide, moisten the spot with sodium thiosulfate and then hold over ammonia. The sensitivity of this reaction is about 1:12,500.

The bromide test can also be carried out as a drop reaction:<sup>18</sup>

**Procedure.** Place a drop of the solution to be tested in the depression of a spot plate and add a microdrop of a 0.1 per cent fluorescein solution and a

microdrop of a mixture of 10 parts glacial acetic acid and 1 part 30 per cent hydrogen peroxide, and then evaporate to dryness over a water bath. A pink to red color appears if bromide is present. A blank test, using a drop of water, is recommended when detecting small quantities of bromide.

**Determination of bromine and bromide.** The reaction of fluorescein with bromine to form eosin may be used for the colorimetric determination of small quantities of bromine and bromide.<sup>19-23</sup> This determination can be carried out even in the presence of large quantities of chloride. Filter paper impregnated with a solution of fluorescein can be used for the estimation of bromide, after converting the latter to free bromine by means of a suitable oxidizing agent;<sup>18</sup> or the estimation can be carried out colorimetrically in the usual manner by employing a solution of fluorescein. The methods used for determining bromide in the presence of 1000 times as much chloride are not always theoretically sound, although empirical conditions have been used such that chlorine and bromine equivalent to amount of bromine present is liberated. The oxidation potential of bromide and chloride are not sufficiently far apart to permit a complete separation by oxidation. It is possible, however, to oxidize all the bromine present in a solution with only very incomplete oxidation of chloride. The halogen can then be converted into the halide and the process repeated until a complete separation is achieved. The determination can also be carried out by passing a mixture of all the bromine and a part of the chlorine into a reagent such as fluorescein dissolved in pyridine which reacts rapidly with bromine and only slowly with chlorine. A more promising method, however, has been proposed by Hahn:<sup>22,23</sup>

**Reagents.** *Fluorescein solution:* Mix 5 g. of fluorescein with 5 ml. of 0.1 N sodium hydroxide solution and dilute to 1 liter.

*Buffer solution:* Prepare approximately N solutions of sodium hydroxide and acetic acid and determine their equivalent ratio by titration with phenolphthalein. To the sodium hydroxide solution add an equivalent quantity of acetic acid and one-tenth to one-ninth of this quantity in excess. This solution has a pH of 5.6-5.5.

**Procedure.** To the unknown solution, add acetic acid or sodium hydroxide until the color with methyl red is the same as that obtained by adding the indicator to the buffer solution of pH 5.6-5.5. To 1 ml. of this solution, add 3 drops of the buffer solution, 1 drop of the reagent, and 1 drop of 0.01 M chloroamine T solution. Allow the mixture to stand for 1-1.5 minutes and stop the oxidation of the halide by adding 1 drop of a solution containing 5 per cent sodium hydroxide and 0.5 per cent sodium hydrosulfite. Compare the resulting color with a series of standards containing 0.0001, 0.0002, 0.0004, 0.0008, 0.0013, 0.002 mg. of bromine. For larger quantities of bromine, increase the amount of reagent used.

**Detection of bromate.** Hahn<sup>24</sup> has used a method for detecting bromate which is based upon the conversion of the bromate to bromine and its subsequent reaction to fluorescein.

**Reagent.** Dissolve 0.1 g. of fluorescein in 5 ml. of 0.1 N. sodium hydroxide and dilute to 1 liter.

**Procedure.** To 1 ml. of the solution to be tested add 0.1 ml. of fluorescein and a little solid oxalic acid. Heat to boiling, cool, and add 1-3 drops of 0.1 M chloroamine T. Compare the color change with a blank test. This test can be obtained with 10γ of potassium bromate in the presence of 0.1 g. of potassium chlorate.

**Detection and determination of ozone.** Benoist<sup>25</sup> has used very dilute solutions of fluorescein (1:1,000,000) as a very sensitive reagent for the estimation of ozone. This determination is based upon the fact that the fluorescent color of the reagent is quantitatively dissipated by ozone in a reaction in which two moles of ~~ozone~~ react with one mole of fluorescein. As little as 1γ of ozone can be determined by this method.

Mache<sup>26</sup> recommends the iodometric determination of ozone for quantities greater than 40 mg. per liter,<sup>27</sup> but claims that superior results are obtained for small quantities by means of Benoist's method, provided the pH is rigorously fixed. Heller<sup>28</sup> has used a slightly modified form of Benoist's fluorescein method, but states that it is not completely satisfactory. Errors arise from the fact that the ratio of ozone to fluorescein destroyed depends upon the pH of the medium, and varies with the amount of fluorescein. It increases as the partial pressure of ozone decreases, thus making results unreliable when this is lower than about ten times the quantity of ozone in air. On the other hand the method appears to be more reliable than an iodometric method, since it is only slightly affected, if at all, by other components of the atmosphere such as nitric oxide, nitrogen dioxide, carbon dioxide, hydrogen peroxide and traces of chlorine.

Masterman<sup>29</sup> has also used fluorescein as a reagent for ozone and hypochlorous acid.

Egorov<sup>30</sup> has determined ozone by a method which depends upon the oxidation of the leuco-base to form fluorescein. The method is rapid and sensitive, and the fluorescence is stable in an alkaline solution.

**Reagent.** Dissolve 1 mg. of fluorescein in 1 ml. of 10 per cent sodium hydroxide solution. Add 10 ml. of saturated sodium hydroxide solution and reduce the mixture by shaking with 1 g. of zinc dust until the fluorescence has completely disappeared. Filter, and use the clear filtrate as the reagent.

**Procedure.** Add 1 drop of the reagent to 10 ml. of a 0.5 per cent sodium hydroxide solution contained in a tube, and pass air (or gas containing small quantities of ozone), through the solution at a rate not to exceed 15 liters per hour until the color of the solution matches that of a standard containing 1 part of fluorescein in 100,000,000 parts of water. The ozone in the air is then calculated on the basis that 1 part by weight of fluorescein is produced by 0.96 parts by weight of ozone. This ratio indicates that the oxidation of the leuco-base to fluorescein proceeds at about 25 times the speed of the reaction of fluorescein with ozone to form a colorless compound.

The oxides of nitrogen, hydrogen peroxide, traces of chlorine and small quantities of carbon dioxide do not interfere with this method.

**Detection of oxygen.** Traces of oxygen destroy the fluorescence of adsorbates of the sodium salt of fluorescein (uranin), and consequently can be detected with this reagent. Highly polymerized, well-aged gels of inorganic acids or hydroxides, such as silicic acid or aluminum hydroxide are suitable as adsorbents. These materials must neither be colored nor opaque.<sup>31</sup>

**Detection and determination of hydrogen cyanide.** An intense fluorescence appears when solutions of the leuco-base of fluorescein and copper sulfate are mixed in the presence of small quantities of cyanides. This reaction has been used by Stamm and others<sup>32-34,44</sup> for the detection of cyanides.

**Reagent.** Dissolve 0.01 g. of fluorescein in a mixture of 5 ml. of alcohol, 2 ml. of 33 per cent sodium hydroxide solution and 5 ml. of water. Add a little zinc dust and warm on a water-bath until the solution is decolorized. Dilute with water to 100 ml., then add 100 ml. of alcohol, mix well, and allow the mixture to stand overnight in the dark. Filter and when ready to use dilute 10 ml. of the filtrate with sufficient water to make 200 ml. of solution.

**Procedure.** To 4 ml. of the solution to be tested, add 4 ml. of the above reagent and 3 drops of a 1:2,000 solution of copper sulfate. If cyanides are present an immediate fluorescence appears, either in the cold solution or upon heating the solution to 90° C. This reaction is sensitive to 0.9 mg. of HCN per liter.

Potassium persulfate reacts strongly on warming the mixture for 1-2 minutes, but the color disappears after about 5 minutes. Sodium hypochlorite and chlorine water cause a green fluorescence with a slight pink tint. Bromine water shows a pink color in an alkaline solution. Roozendaal<sup>36</sup> has studied various reagents which have been used for the determination of hydrogen cyanide, such as sodium nitroprusside, picric acid, guaiac resin, phenolphthalin, benzidine, pyrazolidone and fluorescein, and reports that fluorescein is not definitely characteristic but recommends this reagent as the most satisfactory of those listed.

**Detection and determination of arsenate.** Pentavalent arsenic in strongly acid solutions oxidizes iodides to free iodine, and this reaction is complete if the free iodine is fixed by reacting with another reagent. If fluorescein is used for this purpose, the color change of the dye indicates the quantity of arsenate that is present. Since this reaction is an oxidation reaction, it is not specific for arsenate, but in certain limited uses where other oxidizing substances are known to be absent the test is useful for detecting small quantities of arsenates. This reaction has been used by Hahn<sup>37</sup> for the detection of arsenate in arsenite solutions. The only oxidizing substance which is likely to be present in such solutions is ferric iron, and the effect of this can be eliminated by acidifying with an excess of phosphoric acid.

**Reagent.** Mix 0.1 g. of fluorescein with a few drops of sodium hydroxide solution and 50 g. of potassium iodide and dilute with water to 100 ml.

**Procedure.** To 1 ml. of the solution to be tested add 0.2 ml. of the reagent and 0.2 ml. of phosphoric acid, and then heat on a boiling water-bath for 15 minutes. The color of the solution changes, according to the arsenate content, from a greenish-yellow to a brownish-yellow or a reddish-brown. As little as 0.5 per cent of arsenate can be detected by this method, although the color change is more easily observed with 1 per cent of arsenate.

The test can be made more sensitive by shaking the solution with 2 ml. of ether to extract the dye.

By means of this color reaction the quantity of arsenate can be approximately determined by comparison with suitable standards.

**Detection of hydrogen-peroxide.** With fluorescein, under unfavorable conditions of artificial light, hydrogen peroxide can be detected at dilutions of 1:5,000,000, and with ultra-violet light it can be detected at concentrations of 1:10,000,000. The reagent is not likely to prove very useful, however, since it reoxidizes rather rapidly on standing.<sup>38</sup>

**Detection of lead, silver and mercury.** Fluorescein yields with lead ions in a slightly alkaline solution a rose colored precipitate, which can be used to detect 1 part of the lead nitrate in 500 parts of water. The test is carried out as follows:

**Procedure.** To 5 ml. of a solution containing lead ions add 2 drops of a saturated fluorescein solution in aqueous methyl alcohol. Then add ammonium hydroxide or sodium hydroxide dropwise until precipitation occurs. A pink coloration usually appears immediately, and a pale pink or rose colored precipitate soon settles out of the solution. If no interfering ions are present, the supernatant liquid usually remains bright yellow.

This test is satisfactory even in the presence of other cations, provided they are not present in large quantities. Some colored substances, such as ferric or copper salts, may obscure the pink color of the reaction, but when these substances are present in very small quantities the color can still be observed. Mercurous ions interfere, since on the addition of the alkali the solution turns dark and obscures the color. In very dilute solutions, however, the color may be observed before the darkening occurs. The above color reaction appears to be due to the adsorption of the color by lead hydroxide. In the presence of aluminum, magnesium and antimony the pink color appears immediately upon the addition of the reagent, but upon standing the color may be obscured by other precipitates. It is interesting to note that in the presence of some colored ions such as cobalt and nickel, the pink lead hydroxide precipitate settles out when an excess of ammonium hydroxide is used.<sup>39-41</sup>

Silver can be detected by the following procedure:

**Procedure.** To 5 ml. of a solution containing the silver salt, add 1 or 2 drops of a saturated solution of fluorescein in a water-alcohol mixture, and then add dropwise a 4 N solution of sodium carbonate. Exercise great care in avoiding an excess of the reagent, since in this case the color is destroyed. A pink

or rose colored precipitate forms if silver is present. This test is sensitive to 1 part of silver in 500 parts of water.

Mercurous, mercuric, stannous, stannic, ferrous and some colored ions such as ferric and nickel interfere with this test.

A light yellow precipitate is obtained when solutions of mercurous salts are precipitated with 1 N sulfuric acid in the presence of fluorescein.<sup>40</sup> This reaction is not, however, a very sensitive one and offers no useful advantages in the detection of mercury.

**Detection of boric acid.** Boric acid may be detected by the fluorescence which forms with fluorescein. As little as 20% of boric acid can be detected with a 1:10,000 solution of fluorescein.<sup>35,43</sup>

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## FUCHSIN

$C_{20}H_{20}N_3Cl$

Mol. Wt. 319.19

Beil. Ref. XIII, 763, 765.



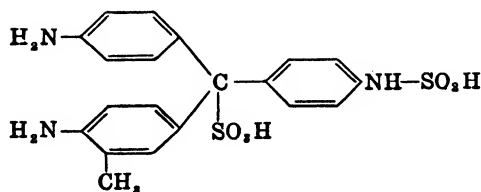
**Use:** Detection of bromide, bromate, sulfite, nitrite, chloride, persulfate, chlorine.

Determination of bromine and copper.

Basic fuchsin is a mixture of rosaniline and *p*-rosaniline hydrochlorides. It consists of lustrous crystals which dissolve in water to yield a red colored solution. The dye is soluble in alcohol and in amyl alcohol.

Acid fuchsin, also known as acid magenta, rubine S, fuchsin S and acid roseine, is a mixture of sodium and ammonium rosaniline di- and trisulfonates. It is a red to reddish-brown powder which is soluble in water.

**Detection of bromide.** The triphenylmethane dye, fuchsin reacts with sulfurous acid to form a colorless compound, which according to Wieland and Scheuing<sup>1</sup> is the N-sulfinic acid of fuchsin leuco-sulfonic acid.



A solution of fuchsin decolorized with sulfurous acid is colored blue by free bromine, due to the formation of a brominated compound. Since neither chlorine or iodine impart a color to a colorless fuchsin sulfurous acid solution the reaction can be used for the detection of small quantities of bromide in the presence of chloride and iodide. Bromides are converted to free bromine by treating with a concentrated solution of chromic acid. This reaction was first used by Deniges<sup>2-6,11</sup> and Guareschi<sup>7-9</sup> for the detection of bromide. The following procedure has been used by Deniges:<sup>11</sup>

**Reagent.** Add 10 ml. of 31.5 per cent sodium bisulfite solution to 1 liter of 0.1 per cent solution of fuchsin. Allow the mixture to stand for 5 minutes and add 20 ml. of concentrated hydrochloric acid. After standing for 1-2 hours, the reagent is ready for use, although it may be still somewhat colored.

**Procedure.** In a test tube, mix 2 ml. of the reagent and 2 ml. of hydrogen peroxide, and then add 1 ml. of chloroform. Next add a little of the aqueous solution to be tested and shake well. The chloroform layer is colored amethyst and shows a strong absorption band in the yellow-orange region with as little as 0.01 mg. of bromine.

Deniges and Chelle<sup>2</sup> have proposed a modification of the earlier procedure<sup>3,4</sup> to eliminate the disturbing effect of nitrite:

**Reagent.** Mix 10 ml. of a 1:1,000 fuchsin solution with 100 ml. of 5 per cent sulfurous acid. After standing for 1 hour the mixture is colorless and ready for use.

**Procedure.** In a test tube, place 5 ml. of the solution containing not more than 1 g. of bromine per liter and add 4 drops of concentrated hydrochloric acid, 4 drops of 10 per cent potassium chromate solution, and 1 ml. of concentrated sulfuric acid. Mix well and immediately immerse the test tube in water cooled to 15-16° C. After 5 minutes add 1 ml. of the fuchsin reagent and 1 ml. of alcohol-free chloroform. Shake vigorously for at least 1 minute and allow to stand. The chloroform is colored pink if bromine is present, and the intensity of the color varies with the quantity of bromine present. Bromine at a concentration of 1 mg. per liter can easily be determined in the presence of 1 g. of sodium nitrite.

Deniges and Chelle<sup>5,6</sup> also proposed the following method for the detection of chlorine and bromine:

**Reagent.** Mix 10 ml. of 0.1 per cent fuchsin solution with 100 ml. of 5 per cent sulfurous acid solution and allow the mixture to stand until colorless.

**Procedure.** Mix 25 ml. of the reagent with 25 ml. of glacial acetic acid and 1 ml. of sulfuric acid. To 5 ml. of this mixture, add from 1 drop to several ml. of the solution to be tested and shake. With free chlorine a yellow color is obtained and with bromine a reddish-violet color. The test may be made somewhat more sensitive by extracting the color with chloroform. In this way 0.05 mg. of chlorine and 0.005 mg. of bromine can be detected.

The bromine test may be satisfactorily carried out by means of a spot test, using paper impregnated with a solution of fuchsin that has been decolorized with sulfurous acid.<sup>10-12</sup>

Lopez<sup>13-15</sup> has used a modification of the Guaraschi<sup>7-9</sup> method for the detection of small quantities of bromide in sodium chloride.

**Procedure.** To 10 ml. of water in a test tube, add 1 drop of a saturated fuchsin solution, and then add a chlorine solution (containing about 0.24 mg.



of chlorine per ml.) dropwise until the mixture is decolorized. This usually requires about 6-8 drops. To 10 ml. of the solution to be tested add 1 drop of the fuchsin solution and twice as many drops of chlorine as previously determined necessary for the decolorization of the fuchsin. In the presence of bromine, a pink color is obtained which, if sufficient bromine is present, turns violet with the formation of a violet precipitate. By this method, 0.1 mg. of potassium bromide can be detected in 10 ml. of a 20 per cent sodium chloride solution.

The reaction is prevented by iodide, sulfite, nitrite, thiosulfate, cyanide, thiocyanate and ferricyanide. Salts which react alkaline, such as borates and phosphates must be neutralized before applying the test. Some investigators recommend the addition of hydrochloric acid, but this seems unnecessary and may possibly be a source of error, since hydrogen chloride often contains hydrogen bromide.

Deniges<sup>16,17</sup> has used fuchsin for the detection of bromine in urine, and Jones<sup>18</sup> has used a similar procedure for the detection and determination of small quantities of bromides in saline solutions and mixtures of halogens.

Nicolas<sup>19</sup> and Montequi and Puncel<sup>20</sup> have used the bromine reaction with fuchsin for the detection of bromate.

**Procedure.** To 2-3 ml. of a solution containing 0.05 g. of fuchsin and 50 ml. of hydrochloric acid in 200 ml. of water, add a few drops of the solution to be tested. A violet-red color appears if bromate is present. The sensitivity of this reaction is 0.002 mg.

Nicola<sup>19</sup> has used this reaction for the detection of bromate in bromide.

**Procedure.** Dissolve 1 g. of the potassium bromide in 20 ml. of water and add a few drops of fuchsin in a sulfurous acid solution. A blue-violet color develops on shaking if bromate is present.

**Determination of bromine.** The color reaction of fuchsin and bromine may be used for the determination of bromine and bromide.<sup>21-25</sup> Fuchsin, decolorized by sulfurous acid and developed with a hypochlorite solution, gives a color with bromine which is suitable for the colorimetric estimation by the use of a series of standards:<sup>25</sup>

**Reagents. Fuchsin solution:** Add 80-90 mg. of sulfur dioxide dissolved in water to 100 ml. of 1 per cent fuchsin solution and dilute to 1 liter. This solution becomes colorless or faintly yellow in 24-36 hours, and may be kept for several days if stored in a cool, dark place.

**Oxidizing solution:** Dissolve 1 g. of calcium hypochlorite containing about 0.4 g. of available chlorine in water and dilute to 500 ml. Mix 0.1 ml. of 1.49 per cent potassium bromide solution and 1 ml. of 25 per cent sulfuric acid. To this mixture in three separate tubes, add 0.2, 0.25 and 0.3 ml. of the oxidizing solution. Add to each 1 ml. of the fuchsin reagent. The oxidizing solution should be of such strength that 1 of the 3 tubes will have a gray-violet color. This tube corresponds to the standard volume of oxidizing solution which

should be used. If necessary, dilute the oxidizing solution so as to give a suitable color in 1 of the 3 tubes.

**Procedure.** Dissolve a quantity of the bromide such that 1 ml. of the solution contains about 0.2 mg. of the bromide ion. Measure 0.1, 0.2, 0.5, 0.8 and 1.0 ml. of the unknown into separate test tubes, and to each add 1 ml. of 25 per cent sulfuric acid, the necessary volume of oxidizing solution, and 1 ml. of the fuchsin reagent. One of these solutions should be gray-violet in color, and contain about 0.1 mg. of bromide in the volume used. This should be checked by transferring the same amount of sample to 3 separate test tubes and treating each in the same way except that to one 0.05 ml. less of the oxidizing solution is added. This solution should be yellow in color. A second tube should be prepared exactly as described above and should duplicate the previous gray-violet color. To the third tube add 0.05 ml. more of the oxidizing solution and this mixture should be distinctly violet in color. Prepare a series of standards containing 0.075, 0.1 and 0.125 mg. of bromide. Dilute each to the volume of the sample solution, and to each add the same reagents as to the sample which gave a gray-violet color, and then compare with that of the sample. This method gives results which are accurate to about 5 per cent.

Bromine, liberated from bromides by the action of chlorine water, forms a violet color in a sulfuric acid solution of basic fuchsin. The intensity of the color formed is proportional to the amount of bromine present.<sup>14,15,26,27</sup> By extracting the color with isoamyl alcohol, small quantities of bromide can be determined colorimetrically. This method may be used to detect 0.007 mg. of bromine. The following method may be used for the determination of bromide in blood:

**Reagent.** Place 100 ml. of 5 per cent sulfuric acid in a 250-ml. flask, and add 10 ml. of a 1 per cent solution of fuchsin. Shake and allow to stand for about 2 hours, after which the solution should be entirely colorless.

**Procedure.** Measure 10 ml. of blood into a 50-ml. porcelain dish, and add 4 ml. of standard sodium bromide solution containing 0.01 mg. of bromide per ml. into a similar dish. To each add 5 drops of 10 per cent potassium hydroxide solution, mix well, and then to each add 0.5 g. of magnesium oxide. The magnesium oxide should be so added as to cover the entire surface of the solution. Cautiously evaporate to dryness over a burner and ash in a muffle furnace. Dissolve the ash in about 30 ml. of 7.5 per cent sulfuric acid and dilute each solution to 40 ml.

Transfer 20 ml. of the sample and standard solution to separatory funnels, and to each add 2 ml. of a freshly prepared 5 per cent solution of chlorine water and 20 ml. of the fuchsin reagent. Shake vigorously and add 5 ml. of isoamyl alcohol. Again shake and allow the layers to separate. For the final determination, compare the color of the isoamyl alcohol extracts.

Various investigators<sup>21,24,28-30</sup> have used various modifications of the fuchsin reaction for the detection and determination of bromides in blood and biological fluids.

**Detection and determination of sulfurous acid.** Sulfurous acid and sulfites may be detected in the presence of thiosulfates and thionates by a method based on the almost instantaneous decolorization of dilute solutions of triphenylmethane dyes by solutions of normal sulfites. Thiosulfite, thionate, bicarbonate and phosphate do not interfere. Mono- or polysulfides must be removed, since they cause a similar decolorization. Votocek<sup>31</sup> has suggested as reagent a solution prepared by mixing three parts of fuchsin containing 0.25 g. per liter with one part of malachite green of the same concentration. This reagent will detect 0.06 mg. of  $\text{SO}_2$  in 1 ml. of solution.

Malinovskii<sup>32</sup> recommends the following procedure for the detection of sulfite in the presence of thiosulfate:

**Reagent.** Dissolve 0.34 g. of fuchsin in 1 liter of water containing 1 g. of sulfuric acid and heat slightly on a water-bath.

**Procedure.** Prepare saturated aqueous solution of the material to be tested and add 15 volumes of water. Add 1 drop of 1 per cent phenolphthalein; and, if the solution is alkaline, carefully neutralize with 0.1 N acetic acid. To 10-15 ml. of the neutralized solution add a few drops of the fuchsin reagent. Decolorization within a few minutes is a certain indication of the presence of sulfite. Thiosulfate does not interfere with these conditions.

Meneghetti<sup>41</sup> recommends a mixture of a 0.02 per cent solution of fuchsin and a 0.007 per cent solution of methyl green for the detection of sulfite.

Kastner<sup>33</sup> has used a method based upon the decolorization of fuchsin for the determination of sulfur dioxide in air.

**Detection and determination of nitrite.** Dubsky and Okac<sup>34,35</sup> have used fuchsin for the detection of nitrite.

**Procedure.** To 2 ml. of the solution to be tested add dropwise a solution containing 10-50 mg. of fuchsin in 100 ml. of solution to impart a perceptible color to the mixture. Then add 1.0 ml. of N hydrochloric acid, and after 10 minutes, a crystal of  $\alpha$ -naphthylamine, phenol or  $\alpha$ -naphthol, and finally make the mixture alkaline with sodium hydroxide or ammonium hydroxide. The reagent is red, and with nitrous acid turns yellow. Upon the addition of phenol a yellow color is obtained; with  $\alpha$ -naphthol a red color; and with  $\alpha$ -naphthylamine a violet color.

Fuchsin is also used in the preparation of permanent color standards in the Greiss diazo reaction with  $\alpha$ -naphthylamine and sulfanilic acid.<sup>36,37</sup>

**Detection of persulfate.** Lenz and Richter<sup>38</sup> use fuchsin in a reagent for the detection of persulfates:

**Reagent.** Dissolve 0.05 g. of fuchsin and 12.5 g. of sodium acetate in 100 ml. of water.

**Procedure.** Add the reagent dropwise to a few ml. of the solution to be tested and heat. Sodium perborate and percarbonate readily decolorize the

reagent, and the addition of water does not restore the color. Acetic acid gives a yellow color. Ammonium persulfate decolorizes the reagent only with difficulty and an excess of water or the addition of acetic acid will not restore the color.

Potassium perchlorate has no effect.

**Determination of copper.** Reed and Cummings<sup>39</sup> have used fuchsin in a polarographic method for the detection of copper in plant materials. The best polarographic curves were obtained with a sodium citrate buffer solution of pH 3.8-4.2 with the addition of 1 ml. of 0.05 per cent acid fuchsin to every 10 ml. of the buffer solution.

**Detection of chlorine.** Filter paper immersed in a solution of acid fuchsin is red in color, but this changes to yellow when treated with chlorine. By converting chlorides to free chlorine through the action of potassium permanganate and sulfuric acid, as little as 0.05 mg. of the chloride can be detected. Bromine, nitrite, hypochlorite and hypobromite interfere.<sup>40</sup>

A 0.01 per cent solution of fuchsin in 4.5 per cent sulfuric acid is a suitable reagent. This reagent gives a yellow coloration with as little as 50 $\gamma$  of chlorine in 5 ml. of solution.<sup>5,40</sup> A violet color is obtained when this reagent and a little solid potassium bromide is added to an acetic acid solution containing chlorine. The sensitivity of this reaction is 1:200,000,000.<sup>42</sup>

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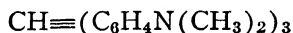
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### HEXAMETHYLTRI-*p*-AMINOTRIPHENYLMETHANE

Synonym: Leuco-crystal violet

$C_{25}H_{31}N_3$

Mol. Wt. 373.50 Beil. Ref. XIII, 315 (100).



**Use:** Detection of chlorine.

Hexamethyltri-*p*-aminotriphenylmethane is a white crystalline solid melting at 173° C.

**Preparation:** Dissolve 25.4 g. of tetramethyldiaminodiphenylmethane in 19.5 ml. of concentrated hydrochloric acid and pour into a mixture of 500 ml. of water, 500 g. of ice and 30 ml. of glacial acetic acid. Stir mechanically until the temperature reaches 0° C. and then add in a thin stream 24 g. of lead peroxide that has been mixed to a thin paste with water. The lead peroxide is freshly prepared by adding a hot filtered solution of bleaching powder to a solution containing the calculated quantity of lead acetate and then washing out the excess bleaching powder. Stir for about 20 minutes and add an aqueous solution containing 30-32 g. of sodium sulfate. Filter and neutralize the blue filtrate with sodium hydroxide. Filter off the grayish-blue precipitate and dry on a porous plate.

Mix 16.2 g. of this product (tetramethyldiaminobenzhydrol) with 9 g. of dimethylaniline and 40 ml. of glacial acetic acid and heat on a water-bath with the gradual addition of 40 ml. of water. Allow the mixture to stand for one-half hour, and then add an additional 40 ml. of water and again heat, this time for 2 hours. Filter the leuco-base and wash with water. Dry on a porous plate and recrystallize from a mixture of benzene and ligroin.<sup>1,2</sup>

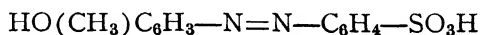
**Detection of chlorine.** A solution of hexamethyltri-*p*-aminotriphenylmethane in hydrochloric acid produces an immediate violet color when added to water containing as little as 0.03 p.p.m. of chlorine. Nitrites interfere with this reaction, but to a lesser extent than when the starch iodide test is used.<sup>3</sup>

1. W. Michler and Ch. Dupertius, *Ber.* **9**, 1900 (1876).
2. M. Nathansohn and P. Müller, *Ber.* **22**, 1879 (1889).
3. G. A. LeRoy, *Compt. rend.* **163**, 226-8 (1916); *C.A.* **11**, 507 (1917).

**2-HYDROXY-5-METHYLAZOBENZENE-4-SULFONIC ACID** $C_{13}H_{12}O_4N_2S$ 

Mol. Wt. 292.29

Beil. Ref. XVI, 273.



**Use:** Detection and determination of hafnium and zirconium.

This reagent consists of light brown leaves, which have a glistening appearance. It is easily soluble in cold water, but is insoluble in cold alcohol. It decomposes on heating.

**Preparation:** Dissolve 8 g. of sodium hydroxide, 32 g. of sulfanilic acid, and 12.1 g. of sodium nitrite in 200-300 ml. of water. Cool with ice and add to a cold solution of 43-45 g. of 30 per cent hydrochloric acid. Allow the mixture to stand 15 minutes and pour into a strongly alkaline solution containing 20 g. of *p*-cresol. Allow to stand for a short time and acidify with concentrated hydrochloric acid. Filter, and dissolve the precipitated salt in the least possible quantity of hot water, and then precipitate the free acid with concentrated hydrochloric acid. Recrystallize from dilute hydrochloric acid.<sup>1</sup>

**Detection and determination of zirconium and hafnium.** Zirconium and hafnium are quantitatively precipitated from an acid solution by the addition of an aqueous solution of 2-hydroxy-5-methylazobenzene-4-sulfonic acid.<sup>2,3</sup> This reaction may be used for the detection and determination of zirconium and hafnium, and for the separation of these metals from iron, aluminum, the rare earths, thorium, antimony, bismuth, molybdenum, uranium, manganese, tin, and titanium.

**Procedure.** Add a few drops of a 1 per cent aqueous solution of the reagent to 5 ml. of a hydrochloric acid or nitric acid solution containing zirconium or hafnium salts. A precipitate forms even at dilutions of 1:1,000,000.

Fluoride, silicofluoride, and sulfate, and citric, tartaric, oxalic and other acids which form complexes with zirconium and hafnium interfere.

The zirconium and hafnium precipitates are converted to  $Zr(OH)_4$  and  $Hf(OH)_4$  by treatment with alkali hydroxides.

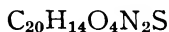
Zirconium and hafnium are separated from tin and titanium with this reagent by adding an alkali chloride to the solution from which precipitation occurs.

The reagent is not satisfactory for the detection of thorium.<sup>4</sup>

1. E. Nolting and O. Kohn, *Ber.* **17**, 355 (1884).
2. V. I. Kuznetsov, *J. Applied Chem. (U.S.S.R.)*, **13**, 1257-61 (1940); *C.A.* **35**, 2092 (1941).
3. V. I. Kuznetsov, *Akad. Nauk. U.S.S.R., Trudy Vsesoyuz Konferentsii Anal. Khim.* **1**, 81-8 (1939); *Khim. Referat. Zhur.* **2**, 57-8 (1940).
4. P. Wenger and R. Duckert, *Helv. Chim. Acta.* **25**; 1110-14 (1942); *C.A.* **37**, 575 (1943).

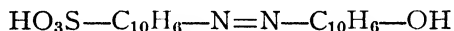
## 2-HYDROXYNAPHTHALENE-1-AZONAPHTHALENE-4-SULFONIC ACID

Synonym: The sodium salt is known as Fast Red A



Mol. Wt. 378.37

Beil. Ref. XVI, 287.



**Use:** Determination of potassium.

2-Hydroxynaphthalene-1-azonaphthalene-4-sulfonic acid consists of red-brown needles, which are only slightly soluble in water, but are easily soluble in alcohol and almost insoluble in ether.

**Preparation.** 2-Hydroxynaphthalene-1-azonaphthalene-4-sulfonic acid is prepared by diazotizing naphthionic acid and coupling with  $\beta$ -naphthol in an alkaline solution.<sup>1</sup>

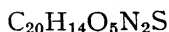
**Determination of potassium.** Tischer<sup>2</sup> has determined potassium indirectly after precipitating as potassium cobaltinitrite by determining the nitrite in the precipitate colorimetrically with sodium naphthionate and  $\beta$ -naphthol. 2-Hydroxynaphthalene-1-azonaphthalene-4-sulfonic acid has been suggested as a color standard in this procedure.<sup>3</sup>

1. P. Griess, *Ber.* **11**, 2199 (1878).

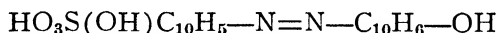
2. J. Tischer, *Biochem. Z.* **238**, 148-61 (1931); *C.A.* **25**, 5641 (1931).

3. J. Tischer, *Mikrochemie, Festschr. Hans Molisch.* 418-35 (1936); *C.A.* **31**, 4229 (1937).

## 2-HYDROXYNAPHTHALENE-AZO-2-HYDROXYNAPHTHALENE-4-SULFONIC ACID



Mol. Wt. 394.37



**Use:** Detection of aluminum and fluorine.

**Detection of aluminum.** Aluminon, alizarinsulfonic acid and morin have been used for the detection of aluminum, but this application is limited, since beryllium also gives reactions with these substances.

Bourstyn<sup>1</sup> has suggested the use of this dye for the detection of aluminum in the presence of beryllium, which gives no reaction with it.

**Procedure.** Adjust the pH of the solution to be tested to about 4.5 with the aid of acetic acid-sodium acetate buffer. To 10 ml. of this solution add 0.5-1.0 ml. of a 1 per cent alcoholic solution of the reagent. A reddish-orange fluorescence appears under ultra-violet light with as little as 0.0002 equivalents of aluminum. Beryllium, even in fairly concentrated solution, gives no similar reaction.

Cobalt, iron and nickel interfere and are removed by boiling with 4 N sodium carbonate and filtering. Zinc and the alkaline earths do not interfere.

The fluorescence caused by aluminum and the reagent is destroyed by the addition of a fluoride, and consequently this reaction can be used for the detection and determination of fluoride. The procedure is similar to that used with alizarinsulfonic acid and zirconium chloride.

1. M. Boursstyn, *Bull. soc. chim.* **8**, 540-1 (1941).

## INDIGO CARMINE

Synonym: Sodium salt of 5,5'-Indigodisulfonic acid, soluble indigo blue  
 $C_{16}H_8O_8N_2S_2Na_2$  Mol. Wt. 466.35 Beil. Ref. XXV, 304.  
 $[NaSO_3-C_6H_3(NH)CO=C]_2$

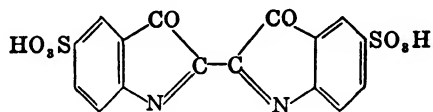
**Use:** Detection of bromate, chlorate, dichromate, ferricyanide, hypochlorite, sulfite and titanium.

Determination of chlorine, ferricyanide, iron, nitrate, oxygen and permanganate.

Indigo carmine is a dark blue powder. It is sparingly soluble in water, with which it yields a deep blue solution. It is almost insoluble in alcohol. The commercial product is often obtained in the form of a paste with water, and the dye content varies according to the specifications or requirements of the consumer. The paste almost invariably contains sodium chloride or sodium sulfate which has been used for "salting out" the dye.

**Preparation:** Mix 6 g. of indigo with 120 g. of concentrated sulfuric acid and some purified sand, and heat on a water-bath for approximately 90 minutes. Pour the mixture into water and filter while hot. Add sodium carbonate to the filtrate until the sodium salt is nearly salted out. Heat to boiling, and allow the mixture to cool. Collect the crystals by filtration, and wash, first with a solution of sodium acetate, and then with alcohol. Purify the product by redissolving in boiling water. Cool, filter, and wash as before.<sup>1</sup>

**Reactions with oxidizing substances.** Many oxidizing substances, such as ferricyanide, ferric salts, permanganate, nitric acid, and chlorate convert the blue dye, indigo carmine, into the yellow disulfodehydroindigo.<sup>2</sup>



This reaction, with the accompanying change of color, can be used for the detection and determination of a number of these substances. The gram equivalent of indigo carmine, used as a reducing agent, corresponds to one half of the gram molecular weight of the compound:

$$\frac{C_{16}H_8N_2O_8S_2Na_2}{2} = 233.18 \text{ g.}$$

**Detection of ferricyanide.** Indigo carmine in a sodium carbonate solution is oxidized by ferricyanide to form pale yellow disulfodehydroindigo. This



reaction is very sensitive, and can be used for detecting ferricyanide in the presence of ferrocyanide.<sup>3,4</sup>

**Procedure.** In one test tube place 3 ml. of the solution to be tested, and in another test tube place 3 ml. of pure water. To each add 10 drops of saturated sodium carbonate solution, and 2-3 drops of a 0.02 per cent indigo carmine solution. The blue color of the solution containing the ferricyanide soon disappears, while that of the water sample remains for a longer period.

As little as 3-5 $\gamma$  of potassium ferricyanide can be detected in 3 ml. of solution by this reaction. 10 $\gamma$  of ferricyanide can be detected in the presence of 300 $\gamma$  of ferrocyanide.

The use of indigo carmine for the detection of ferricyanide, however, is restricted by the fact that other oxidizing agents behave similarly.<sup>24</sup>

**Determination of ferricyanide.** The above reaction may also be used for the titrimetric determination of ferricyanide.<sup>3,5,6</sup> When a standard solution of indigo carmine is added to a solution of a ferricyanide that has been made alkaline with sodium carbonate, the blue color is discharged as long as any ferricyanide is present, and the end-point is indicated by the appearance of a greenish color when a drop of the blue reagent solution in excess is added to the yellow solution containing the disulfodehydroindigo.

**Reagent.** To prepare a 0.01 N solution of indigo carmine, dissolve 2.3318 g. of the sodium salt or 2.1111 g. of the free acid in water and dilute to 1 liter. For a sharp end-point, the solution should not be more concentrated than 0.001 N, and this may be prepared by diluting the more concentrated solution.

**Procedure. Standardization of the reagent:** Prepare a 0.01 N solution of potassium ferricyanide by dissolving 3.292 g. of the pure salt in sufficient water to make 1 liter of solution. This should be freshly prepared each day.

In a test tube place 2 ml. of 0.001 N potassium ferricyanide, prepared by diluting the above solution, and add 1 ml. of a saturated solution of sodium carbonate, and then titrate from a microburet with 0.001 N indigo carmine solution until the color changes from yellow to a greenish hue. Calculate from the volume of the reagent used, the titer of the indigo carmine solution. Apply an indicator correction of 0.03 ml. of 0.001 N solution for each 5 ml. used.

**Determination of ferricyanide:** Place 2 ml. of the ferricyanide solution and 1 ml. of a saturated solution of sodium carbonate in a test tube, and titrate with the standardized indigo carmine solution to the appearance of a greenish color.

One ml. of 0.001 N indigo carmine = 0.3292 mg.  $K_3Fe(CN)_6$ .

**Determination of permanganate.** Permanganate may be determined in much the same manner as ferricyanides by titrating with a standard solution of indigo carmine. The determination, however, is usually carried out in an acid solution rather than in one containing sodium carbonate.<sup>3</sup>

**Reagent.** Prepare a 0.01 N solution of indigo carmine by dissolving 2.3318 g. of the sodium salt or 2.1111 g. of the free acid in sufficient water to make 1 liter of solution. Prepare a 0.001 N solution of the reagent by diluting the more concentrated solution with water.

**Procedure.** *Standardization of the reagent:* Place 2 ml. of the indigo carmine solution in a test tube and acidify with 1 ml. of 1:5 sulfuric acid, and then titrate with 0.001 N potassium permanganate solution to the appearance of a pure yellow color. One ml. of 0.001 N  $\text{KMnO}_4$  solution = 0.23318 mg. of the sodium salt of indigo carmine or 0.2111 mg. of the free acid.

*Determination of permanganate:* Place 2 ml. of the standardized reagent in a test tube and acidify with 1 ml. of 1:5 sulfuric acid, and then titrate with the solution containing the permanganate to the appearance of a pure yellow color. From the titer of the reagent solution, and the amount of the permanganate solution used, calculate the amount of permanganate present.

**Determination of iron.** Small quantities of iron may be determined by means of a microtitration employing very dilute solutions of potassium permanganate, but according to Mika<sup>7</sup> the accuracy of this method depends upon the value of the indicator correction, and the accuracy decreases with an increase in this value. With 0.001 N potassium permanganate, this correction is about 0.12 ml. for each 5 ml. of the solution used. More accurate results are claimed by Korenman<sup>3</sup> by using a measured excess of standardized potassium permanganate, then reducing with a measured volume of indigo carmine solution, and finally back-titrating the excess of the latter with more of the standard permanganate. The indicator correction for indigo carmine is only about 0.03 ml. of 0.001 N solution for each 5 ml. used as compared to 0.12 ml. for the same volume of permanganate solution.

**Reagent.** Prepare a 0.001 N solution of indigo carmine and standardize as described in the preceding section on the determination of permanganate.

**Procedure.** To a weakly acidified solution of the ferric salt to be analyzed, add a slight excess of standardized 0.001 N (or weaker) potassium permanganate solution, then 1-2 ml. of standardized indigo carmine solution, and titrate the excess of the latter with more of the 0.001 N potassium permanganate solution to the appearance of a pure yellow color.

The iron content of the unknown solution is calculated from the following equation:

$$[(V_1 + V_2)N - V_3 \times N_1] \times 55.84 = \gamma \text{Fe}^{++}$$

$V_1$  = Added volume of potassium permanganate solution.

$V_2$  = Volume of same solution required to oxidize excess indigo carmine solution.

$V_3$  = Volume of indigo carmine solution.

$N$  = Normality of the potassium permanganate solution.

$N_1$  = Normality of the indigo carmine solution.

55.84 =  $\gamma$ -equivalent of iron.

**Detection of chlorate, bromate, and dichromate.** A solution of indigo carmine is decolorized by sulfurous acid in the presence of a chlorate. Autenrieth<sup>8</sup> and Korenman<sup>9</sup> have used this reaction as the basis for a method for detecting chlorate and sulfite.

**Procedure.** To 2 ml. of a neutral or acid solution to be tested, add 0.5 ml. of a saturated solution of sodium sulfite, 3-4 drops of an aqueous solution of indigo carmine, and 1 ml. of 3 N hydrochloric acid. The blue color disappears if chlorates are present. The sensitivity of this reaction is 0.4% potassium chlorate in 2 ml. The limiting concentration is 1:5,000,000.

This reaction may also be used as a spot test for chlorates.

**Procedure.** Mix 1 drop of the chlorate solution, 1-2 drops of 0.02 per cent indigo carmine solution, 1 drop of a saturated solution of sodium sulfite, and 1 drop of 3 N hydrochloric acid. The color is discharged with as little as 0.02% of potassium chlorate in 0.03 ml. of solution. The limiting concentration is 1:160,000.

Bromate and dichromate also give this test. As little as 0.66% of bromate in 2 ml. can be detected in a test tube reaction, and 0.24% in 0.03 ml. (1 drop) by means of a drop reaction. Dichromate can be detected in quantities as low as 0.66% in 2 ml. by the same reaction. The dilution limit is 1:3,000,000. As little as 0.02 mg. of potassium chlorate or bromate can be detected in the presence of as much as 10 mg. of potassium iodate.

Potassium permanganate and hypochlorite decolorize indigo carmine in the absence of sulfite. Ferricyanide and potassium iodate cause a change in color in the presence of sulfite from blue to green.

Hunt<sup>10</sup> has used a modification of the method of Korenman<sup>9</sup> for the detection of minute quantities of chlorate.

**Reagent.** The reagent is prepared by mixing the following:

- 20 drops (1 ml.) of 3 N hydrochloric acid,
- 16 drops (0.864 ml.) of 20 per cent sodium sulfite, and
- 1 drop (0.063 ml.) of 0.02 per cent indigo carmine solution.

These solutions should be delivered from a standard buret.

**Procedure.** Two sets of the indicator solution must be prepared, the chlorate being added to one and an equal amount of water to the other. A stop-watch is used to time the change in color, and a positive action can only be accepted when the chlorate gives constantly a more rapid discharge of color than does the distilled water in the control tube. Since the color of the indicator is discharged by exposure to air, an interval of 3 minutes is allowed for the discharge of the color in the tube containing the chlorate. The reaction time decreases with an increase in the concentration of the chlorate.

Indigo carmine mixtures are more sensitive as reagents for chlorate than those containing either methyl red or methyl orange. The above reagent gives a positive reaction with 1 drop (0.06 ml.) of a 0.001 per cent solution of sodium chlorate.

**Detection of sulfites.** Sulfite is detected by making use of the fact that the color of a solution containing indigo carmine and potassium chlorate disappears in the presence of sulfites.<sup>8,9</sup>

**Procedure.** Mix 2 ml. of a solution containing a sulfite with 0.5 ml. of a saturated solution of potassium chlorate, and then acidify with 1 ml. of 3 N hydrochloric acid. After adding 2-3 drops of a 0.02 per cent aqueous solution of indigo carmine, the blue color disappears quickly in the presence of sulfites. By this method, 2.5γ of SO<sub>2</sub> may be detected in 2 ml. of solution.

By means of a drop method, 0.5γ of SO<sub>2</sub> can be detected in 0.03 ml. of solution.

**Determination of nitrates.** Nitrate can be determined by means of a method which depends upon the oxidation of blue indigo carmine to light yellow isatinsulfonic acid.<sup>11</sup> The formation of this color is not suitable for the colorimetric determination of small quantities of nitrate, but a satisfactory determination has been based on the principle of microtitration. The determination is carried out by titrating a solution of nitric acid in sulfuric acid with a standard solution of indigo carmine until the color of the solution changes to a bluish green.

A method for titrating nitrate in bismuth salts with the use of indigo carmine has been proposed by Simmons,<sup>12</sup> Ferrey,<sup>13</sup> and Villegas de Bollini.<sup>14</sup>

**Preparation of standard indigo carmine solution.** Dissolve 0.5 g. of indigo carmine in water and filter, and to the filtrate add 50 ml. of concentrated sulfuric acid and dilute to 1 liter. Standardize against a solution containing 1 g. of pure potassium nitrate dissolved in 1 liter of water. Pipet an aliquot of the standard nitrate solution into a 250-ml. flask and dilute with water to 25 ml. Then add 25 ml. of concentrated sulfuric acid in two equal portions, and immediately titrate the resulting solution with the indigo carmine solution to the appearance of a permanent bluish-green tint.

A curve is then plotted using mg. of N<sub>2</sub>O<sub>5</sub> and the number of ml. of indigo carmine solution as the coordinates.

**Procedure.** Dissolve 0.5-1.0 g. of the bismuth salt to be analyzed in 25 ml. of distilled water, and add 25 ml. of concentrated sulfuric acid in two equal portions as in the standardization of the indigo carmine, and immediately titrate with the standard indigo carmine solution. The titration should not require more than 40 seconds to insure accurate results.

The quantity of nitrate is determined by reference to the standardization curve obtained as described above.

Excellent results are claimed with 5 ml. of solution containing 0.1 per cent of nitrate. The method is not satisfactory, however, with bismuth salicylate, tannate, or gallate.

**Determination of active chlorine.** Hausner<sup>22</sup> has used indigo carmine in a method for determining active chlorine in bleach liquors.

**Reagent.** Dissolve 0.85 g. of sodium thiosulfate,  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ , and 0.14 g. of indigo carmine in 1 liter of water.

**Procedure.** Pour a definite volume of the bleach liquor into a graduated, stoppered cylinder and add 1-2 drops of acetic acid. Add the reagent in small portions, with thorough shaking after each addition, until a bluish-green color is obtained. By a similar procedure, employing solutions of known chlorine content, the cylinder may be calibrated to read in grams of available chlorine per liter.

**Detection of hypochlorites.** Karaoglanov<sup>15,16</sup> has used the following principle to detect hypochlorite in the presence of chlorate and perchlorate: when passed through a 2 N acetic acid solution containing hypochlorite, hydrogen gas carries over sufficient hypochlorous acid to decolorize a dilute solution of indigo carmine. Nitric, chloric, and perchloric acids do not interfere.

**Detection of nitrite, ozone, and hydrogen peroxide.** An aqueous solution of indigo carmine which has been acidified with hydrochloric acid and just decolorized with an alkali sulfide is colored blue by treatment with nitrite, ozone, and hydrogen peroxide.<sup>17,18</sup>

**Detection of titanium.** Knecht<sup>19-21</sup> has used a solution of Rochelle salt which has just been colored blue with indigo carmine as a reagent for titanium. The test is obtained by heating this solution and adding a solution of tervalent titanium salt dissolved in hydrochloric acid. The color of the reagent is discharged with as little as 0.04 mg. of titanium. The color is restored on shaking in air.

**Determination of oxygen.** Oxygen can be determined by passing a stream of the gas through an alkaline solution of sodium hydrosulfite,  $\text{Na}_2\text{S}_2\text{O}_4$ , containing indigo carmine at the rate of 0.5 liter per minute until the color of the solution is intermediate between that of two comparison solutions. From the time required, the oxygen concentration may be read from a previously calibrated curve. Acid gases interfere in concentrations exceeding 1.0 per cent, and also unsaturated hydrocarbons if the concentration is greater than 10 per cent.<sup>23</sup>

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3. I. M. Korenman, *Mikrochemie.* **18**, 31-38 (1935).
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## IODINE GREEN

$C_{27}H_{35}N_3Cl_2 \cdot ZnCl_2$

Mol. Wt. 608.77

Color Index, 686.

**Use:** Detection of ferricyanide.

Iodine green consists of dark green, hard lumps. It dissolves in water with the formation of a blue-green color.

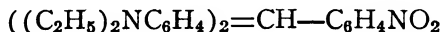
**Preparation:** Iodine green is prepared by the action of methyl iodide or methyl chloride on rosaniline or Hoffmann's violet.

**Detection of ferricyanide.** Ferricyanide may be detected by a reaction which is based upon its ability to oxidize the colorless leuco-derivative of iodine green to the colored dye. According to Lapin<sup>1</sup> excellent results are obtained using this reagent.

1. L. N. Lapin, *Trudy Uzbekskogo Gosudarst. Univ. Sbornik Rabot Khim.* **15**, 150-68 (1939); *C.A.* **35**, 4305 (1941).

## LEUCO-NITRODIAMOND GREEN

Synonym: Leuco-*o*-nitrobrilliant green



**Use:** Detection of gold and thallium.

This compound is an orange-yellow crystalline solid which melts at 108-9° C. It should be preserved in a dark, well-stoppered bottle.

**Preparation:** Mix 20 g. of freshly distilled diethylaniline with 5 g. of *o*-nitrobenzaldehyde and 7.5 g. of anhydrous oxalic acid, and warm on a water-bath for 5 hours with stirring. Add to the melted reaction mixture an excess of 0.2 N sodium hydroxide, and distill with steam to remove the excess diethylaniline. Pour the liquid from the precipitated reagent, and wash carefully with water and then crystallize twice from hot alcohol.<sup>1</sup>

**Detection of thallium.** Thallium may be detected by a method based on the oxidation of thallos salts in an alkaline solution with potassium ferricyanide to thallic hydroxide, which in turn reacts with a solution of leuco-nitro diamond green in acetic acid to give an intense blue-green color. The test also depends upon the solubility of thallos hydroxide and the insolubility of thallic hydroxide.<sup>2,3</sup>

**Procedure.** To the solution to be tested add 5-6 drops of sodium hydroxide solution and 3 drops of a saturated solution of potassium ferricyanide. Mix carefully and filter on a microfilter and wash 3-4 times with water. Treat the precipitate of thallic hydroxide on the filter with a few drops of a solution prepared by dissolving 0.1 g. of the reagent in 5 ml. of acetic acid. An intense blue-green color forms if thallium is present. This reaction will detect 0.01 $\gamma$  of thallium in 0.1 ml. of solution. The reaction is sensitive to 1 part of thallium in 10,000,000 parts of solution.

The following procedure may be used in the presence of other cations.

**Procedure.** To 0.2-0.3 ml. of the solution to be tested, add 0.2 ml. of 2 N sodium sulfate solution. Filter, and to the filtrate add 0.5 ml. of 0.5 N sodium hydroxide solution. Filter, and to the filtrate add 2 to 3 drops of a saturated solution of potassium ferricyanide. Filter, wash the precipitate 5-8 times with water, and add a solution of the reagent in acetic acid. The blue-green color appears if thallium is present.

The following ions do not interfere: calcium, barium, strontium, magnesium, aluminum, manganese, nickel, cobalt, lead, chromium, iron, copper, zinc, silver, bismuth, thorium, uranium, cerium, antimony and tin. As little as 0.25 $\gamma$  of thallium can easily be detected when mixed with 500 $\gamma$  of zinc, chromium, cerium, cobalt, copper and uranium.

**Detection of gold.** A solution containing auric gold can be detected with a chloroform extract of leuco-nitrodiamond green in acetic acid. The reaction is based upon the oxidation of the colorless leuco compound to the green dye. This reaction when carried out as a test tube procedure can be used to detect  $5 \times 10^{-7}$  g. of gold at a dilution of 1:20,000,000. By a spot test as little as  $7 \times 10^{-9}$  g. of gold can be detected at a dilution of 1:12,600. Thallic and ceric salts interfere but are removed by precipitating with sodium hydroxide. The precipitate is filtered and the filtrate is acidified with acetic acid before applying the leuco-nitrodiamond green test. The chloroplatinate ion is precipitated with potassium chloride, and iron is rendered harmless by the addition of sodium fluoride.<sup>4</sup>

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**LEUCO-MALACHITE GREEN** $C_{23}H_{26}N_2$ 

Mol. Wt. 330.44

Beil. Ref. XIII, 275.

**Use:** Detection of cerium, ferricyanide and iridium.

Determination of gold.

Leuco-malachite green is a crystalline solid melting at 102° C. It is insoluble in water, moderately soluble in alcohol and soluble in ether and benzene.

**Preparation:** Fuse 10 g. of zinc chloride in an evaporating dish, cool, and reduce to a powder. Add this to a mixture of 25 g. of freshly distilled dimethylaniline and 10 g. of freshly distilled benzaldehyde. Heat the mixture in an evaporating dish on a water bath with frequent stirring for about 4 hours. Add hot water to the viscous mass and transfer the resulting liquid to a 500-ml. flask and distill with steam. When drops of oil no longer come over, interrupt the distillation and allow the liquid to cool. Pour off the liquid and wash the residue several times with water. Drain the water from the material in the flask and dissolve by adding alcohol and warming on a water bath. Filter and allow the filtrate to stand overnight in a cool place. Collect the crystalline precipitate of the base by filtration, wash with alcohol, and dry in air on several sheets of filter paper. The yield is increased by evaporating the mother liquor until more crystals separate. If the base separates as an oil instead of as crystals, an insufficient quantity of alcohol has been used. In such case, add a little more alcohol and heat the mixture until the oil dissolves.<sup>1,2</sup>

**Detection of cerium.** Cerous hydroxide is converted into ceric hydroxide as a result of auto-oxidation upon exposure to air. Ceric hydroxide in an acid solution converts the colorless leuco-malachite green into the green dye. These reactions have been used by Kul'berg<sup>3,4</sup> as the basis for a very sensitive test for cerium.

**Reagent.** The reagent is a 1 per cent solution of leuco-malachite green in 2 per cent sulfuric acid.

**Procedure.** Make the solution to be tested alkaline with a little N sodium hydroxide to form cerous hydroxide. Filter, wash the precipitate with water, and apply a drop of the reagent solution. A blue green to green color appears if cerium is present. This test is sensitive to 0.03γ of cerium. With very small quantities of cerium, best results are obtained by comparing the test with a blank.

Manganese, cobalt, thallium and silver interfere and must be removed before applying the test.

**Detection of iridium.** Iridium may be detected in the presence of other metals of the platinum group by a reaction based on the oxidation of leuco-malachite green by the chloroiridic ion,  $IrCl_6^{-2}$ , in an acid solution:<sup>5</sup>



**Procedure.** Add a few drops of a 1 per cent solution of leuco-malachite green in strong acetic acid to 8-10 ml. of the solution to be tested. If  $\text{IrCl}_6^{-2}$  is present, and the mixture is not contaminated with an excess of other colored products, the green color of malachite green appears immediately. The colored compound is removed by shaking with a few ml. of chloroform. This reaction is sensitive to 1 part of iridium in 6,000,000 parts of water.

The reaction is masked by the presence of free chlorine, ferric halides, and salts of  $\text{H}_2\text{PdCl}_6$ , which are easily removed. The reaction is not affected by the presence of salts of  $\text{H}_2\text{PtCl}_6$ ,  $\text{H}_3\text{RhCl}_6$ , and other soluble salts of rhodium, compounds of bivalent palladium,  $\text{H}_2\text{OsCl}_6$ , and other compounds of tetravalent osmium. One part of iridium can be detected in the presence of 3000 parts of platinum if the latter is contained in a 0.05 per cent solution as the chloro-platinate.

**Determination of gold.** Traces of gold may be determined colorimetrically with the aid of leuco-malachite green in a procedure proposed by Kul'berg.<sup>6,7</sup> In this determination all solutions must be buffered with acetic acid and sodium acetate to a pH of 3.6.

**Reagent.** Add 0.5 ml. of 80 per cent alcohol to 0.05 g. of leuco-malachite green in 5 ml. of alcohol, and boil for 3-5 minutes. Then add 10 ml. of alcohol and 35 ml. of the buffer solution of pH 3.6.

**Standard gold solution:** Prepare a standard solution containing 0.005 mg. of gold per ml., and containing a quantity of copper equal to that of the solution to be analyzed.

**Procedure.** Add 1 ml. of the reagent to the standard solution, and the same quantity of reagent to the solution to be tested, and boil both mixtures for 1-2 minutes. Cool and compare in a colorimeter, preferably with the aid of a yellow light filter. By this method 0.003 mg. of gold in 10 ml. can be determined.

To determine smaller quantities of gold in the presence of copper, extract prepared solutions with chloroform and proceed with the colorimetric determination of the extracts as described above. In this way, 0.000038 per cent of gold in commercial copper sulfate and 0.000003 per cent gold in copper coins can be determined.

**Detection of ferricyanide.** Ferricyanides can be detected through their ability to oxidize colorless leuco-malachite green to the green dye. To make the test, treat the sample with a 1 per cent solution of leuco-malachite green in 6 N hydrochloric acid and dilute with water. A green color appears if ferricyanides are present.<sup>8</sup> Other oxidizing agents give the same reaction.<sup>9</sup>

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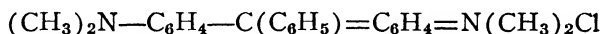
## MALACHITE GREEN

Synonym: Benzaldehyde green, fast green, diamond B green,  
solid green, benzal green

$C_{23}H_{25}N_2Cl$

Mol. Wt. 364.67

Beil. Ref. XIII, 745.



**Use:** Detection of sulfite and tungsten.

Malachite green is a violet-green crystalline solid which exhibits a bronze luster. It is soluble in water and alcohol.

**Preparation.** *Leuco-base:* For preparation of the leuco-base, see above.

*Malachite green:* Place 11 g. of the leuco-base of malachite green in a 1.5-liter round-bottom flask and dissolve in 80 ml. of 2 N hydrochloric acid. Dilute with 800 ml. of water, and cool the diluted solution in ice. While still cooling, add in small portions and with shaking a suspension of 9 g. of lead dioxide in 30 ml. of water.

Filter, and to the filtrate add a clear concentrated solution of 12 g. of zinc chloride and precipitate the zinc chloride double salt by the addition of a saturated brine solution. Filter, wash with brine, redissolve in hot water, cool, and salt out as described above.<sup>1</sup>

**Detection of tungsten.** The reduction of malachite green to the colorless leuco-base by titanous chloride in dilute acid solution is catalyzed by hexavalent tungsten. This reaction has been used by Sandell<sup>2</sup> as the basis for a spot test for tungsten.

**Procedure.** To 0.05 ml. of the neutral or 0.1 N hydrochloric acid solution to be tested, add, on a spot plate, 0.01 ml. of 1 per cent titanous chloride solution and 0.01 ml. of a 0.005 per cent aqueous solution of malachite green. Prepare a blank using distilled water instead of the unknown solution. The time of fading in a neutral solution is 4-5 minutes for the blank, but only 3 seconds if the unknown contains only 1 part of tungsten in 100,000 or 1-1.5 minutes for 1 part of tungsten in 500,000. An increase in the acidity of the solution decreases the sensitivity of the reaction.

Tin, arsenic, antimony, bismuth, copper, gold, platinum, lead, thallium, iron, vanadium, uranium and columbium do not catalyze the reduction of malachite green, but those cations which are easily reduced interfere with the test. Molybdenum catalyzes the reaction to a lesser extent than tungsten. Chloride, sulfate, phosphate and tartaric acid increase the reaction velocity between titanous chlor-

ide and malachite green in the absence of tungsten. Fluoride and nitrate must be absent.

**Detection of sulfite.** Sulfites may be detected by a reaction based upon their ability to decolorize malachite green. Thiosulfate, di-, tri- and tetrathionates do not interfere. Mono- and polysulfides decolorize the dye.<sup>3</sup>

**Procedure.** Prepare a solution consisting of 3 parts of a solution of fuchsin containing 0.25 g. of the dye per liter and 1 part of a solution of malachite green of the same concentration. Add several drops of the reagent to 2-3 ml. of the solution to be tested. The mixture is decolorized in the presence of as little as 0.06 mg. of SO<sub>2</sub> per ml.

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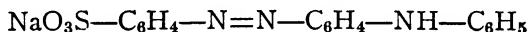
## METANIL YELLOW

Synonym: Victoria yellow, acid yellow R, tropaeolin G, sodium salt of *m*-sulfanilic acid azodiphenylamine

C<sub>18</sub>H<sub>14</sub>N<sub>3</sub>O<sub>3</sub>SNa

Beil. Ref. XVI, 330. Color Index, 138.

Mol. Wt. 375.37



**Use:** Detection of zinc.

Metanil yellow is a brownish-yellow powder which is soluble in water.

**Preparation:** Sulfonate 10 g. of nitrobenzene with 115 g. of fuming sulfuric acid for several hours at 100° C. and convert to the sodium salt in the usual manner. Reduce 75 g. of the sodium *m*-nitrobenzenesulfonic acid by treating with 225 ml. of water, 10 g. of hydrochloric acid, and 100 g. of iron filings. Filter, evaporate the solution to a sp. gr. of 1.18, and precipitate metanilic acid with 50 g. of hydrochloric acid. Mix 15 g. of metanilic acid, 36 ml. of water and 14 g. of hydrochloric acid, and diazotize with a solution of 6.3 g. of sodium nitrite at 7° C. Add the diazotized solution to a solution of 10 g. of diphenylamine and 36 g. of alcohol at 14-15° C., and convert the product to the sodium salt by neutralizing with sodium carbonate.

**Detection of zinc.** Certain aromatic amines and monazo dyes are oxidized by alkali ferrocyanides to form highly colored products, which cause a noticeable color change. Normally the oxidation proceeds very slowly; but if the ferrocyanide which is formed as the reduction product of the ferricyanide is removed by precipitation with zinc ions as insoluble zinc ferrocyanide, the reaction proceeds far more rapidly. Since the precipitated zinc ferrocyanide is deeply colored due to the adsorption of the oxidation product of the dye or the amine, this reaction constitutes a very sensitive test for zinc. Diethylaniline,

orange IV, and metanil yellow are particularly well suited for this reaction. The following procedure using metanil yellow is given by Eegriwe: <sup>1</sup>

**Procedure.** Mix 1 drop of a solution prepared by dissolving 5-10 mg. of metanil yellow in 100 ml. of water with 3 drops of a 2 per cent potassium ferricyanide solution, and add hydrochloric acid until a red color appears. Now add 1 drop of a weakly acidified solution to be tested. The red color completely disappears within 5 minutes if as little as 0.005 mg. of zinc is present.

In a recent critical study of the reagents used for detecting zinc, Wenger, Duckert, and Rieth <sup>2</sup> recommended the use of metanil yellow and potassium ferricyanide, although many ions interfere. By suitable attention to detail they report that 0.03% of zinc can be detected at a dilution of 1:1,000,000.

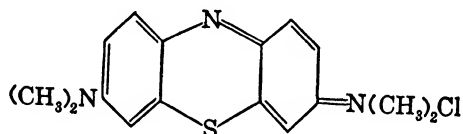
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## METHYLENE BLUE

$C_{16}H_{18}N_3SCl \cdot 3H_2O$

Mol. Wt. 373.89

Beil. Ref. XXVII, 395.



**Use:** Detection of cerium, chlorates, chromium, cobalt, copper, cyanide, ferricyanide, iron, manganese, mercury, molybdenum, oxygen, perchlorate, permanganate, persulfate, rhenium, silver, sulfite, sulfide, tantalum, thiosulfate, tin, titanium, vanadium.

Determination of calcium, chlorate, chromium, iron, magnesium, mercury, molybdenum, oxygen, perchlorate, peroxides, phosphorus, potassium, silver, tin, titanium, vanadium.

Methylene blue consists of dark-green, odorless crystals which have a bronze luster. One gram of the solid dissolves in about 25 ml. of water and 65 ml. of alcohol. It is soluble in chloroform but is insoluble in ether.

**Preparation:** Dissolve 7.6 g. of dimethyl-*p*-phenylenediamine in 70 ml. of N hydrochloric acid and add 35 g. of zinc chloride dissolved in 50 ml. of water. Add with stirring 12 g. of aluminum sulfate dissolved in 20 ml. of water, and then add 15 g. of sodium thiosulfate in 20 ml. of water. To this solution add immediately one-third of a solution containing 16 g. of sodium dichromate in 30 ml. of water. Raise the temperature as quickly as possible to 40° C. and add 6 g. of dimethylaniline dissolved in 8 ml. of concentrated hydrochloric acid. Now add the remainder of the sodium dichromate solution. Increase the temperature quickly to 70° C., and then slowly to 85° C. After standing for 15

minutes, cool the mixture to 50° C. and add 15 ml. of concentrated sulfuric acid to dissolve the precipitate of the inorganic salts. When the mixture is cooled to room temperature, filter with suction and dissolve the residue immediately in 200-300 ml. of boiling water. Filter and add to the filtrate 20 g. of 1:1 zinc chloride solution and 40 g. of powdered sodium chloride. Allow to stand overnight and collect the crystals which separate by filtering with suction. Wash twice with a little ice cold water.<sup>1,2</sup>

**Analytical reactions.** Methylene blue possesses a number of properties which make it useful as a reagent in analytical chemistry. The compound is characterized by great fastness to light; by the stability of its acid solution and the stability of the leuco derivatives; by the relative ease with which it is converted quantitatively into its leuco compound by reducing agents in acid solutions; and by the conversion of leuco compound to methylene blue by oxidizing agents; and by its great tinctorial power. A 0.002 N solution is sufficiently colored to be used for a titration.<sup>3</sup>

The use of methylene blue in qualitative analysis depends upon one of three processes: (a) reducing substances may be detected by converting the blue compound to the colorless leuco derivative; (b) oxidizing agents color the leuco compound, which is formed by reduction with titanous chloride; and (c) neutral salts form characteristic compounds with methylene blue.<sup>4</sup> Among the substances which may be detected with the aid of methylene blue are titanous, molybdenum, vanadous, chromous, tungsten, stannous and cuprous salts. Methylene blue is also reduced by salts of all lower sulfur acids, hydrazine, phenylhydrazine and alkaline pyrogallates. These reductions, however, are not quantitative. Oxidizing agents destroy methylene blue, and the color is not regenerated by the addition of reducing agents. Chlorate, chromate, vanadate and ferric salts are capable of oxidizing the leuco base.<sup>5,6</sup>

**Detection of titanium.** Methylene blue is reduced by titanous chloride to the colorless leuco base. This reaction may be used to detect as little as 0.01 mg. of titanous salt.<sup>4,6,8,9</sup> Dobrolyubskii<sup>7</sup> has used methylene blue in a reaction for the detection of titanium which is based upon the catalytic activity of tetravalent titanium.

**Procedure.** To a solution of the material to be tested in 6 N hydrochloric acid, add 3-4 drops of 0.025 per cent methylene blue solution and a small piece of zinc. If tetravalent titanium is present, the solution is decolorized within 4 minutes, due to its catalytic action. The reaction is very sensitive and can be used for the detection of 0.05% of titanium in a drop of solution. A blank test should be run with methylene blue and zinc to determine the rate of decolorization in the absence of titanium.

By this reaction titanium can be detected in the presence of ferrous, chromic, uranyl and manganous ions.

**Determination of titanium.** Knecht<sup>8-10</sup> and Hibbert<sup>11</sup> have determined titanium by reducing the titanium with zinc and titrating the resulting titanous salt with a solution of methylene blue that has been standardized against pure

titanous chloride. Methylene blue is reduced to the colorless leuco compound as long as titanous salts are present, and at the end-point the color of the solution remains blue upon the addition of a slight excess of the reagent. Neumann and Murphy<sup>12</sup> give the following procedure for the determination of titanium.

**Procedure.** Fuse 1 g. of the sample with potassium hydroxide and sodium peroxide, and dissolve the melt in concentrated hydrochloric acid. Filter and use an aliquot for the determination. If sulfuric or nitric acid is present from the decomposition of the sample, titanium must be precipitated with ammonium hydroxide and redissolved in hydrochloric acid. To the clear solution add 30 ml. of concentrated hydrochloric acid, about 2 g. of zinc dust, and a few pieces of zinc. The reduction requires about 15-20 minutes. Filter the solution into an Erlenmeyer flask into which a stream of carbon dioxide is passed. Add 20 ml. of concentrated hydrochloric acid and suspend in the solution a piece of zinc which is held by a platinum wire passing through a Bunsen valve. Heat the solution for a few minutes, draw the zinc out of the solution, and then add methylene blue solution from a buret whose outlet passes through a Bunsen valve. The reagent is added dropwise until a pale blue color persists. The reagent is prepared by dissolving 3.9-7.8 g. of methylene blue in a liter of solution and standardizing against a titanium solution of known strength.

The method is satisfactory except in the presence of tungsten and columbium.<sup>13</sup> Molstad<sup>14</sup> states that Hibbert's<sup>11</sup> method gives good results except in the presence of vanadium and tungsten, both of which reduce methylene blue.

Leutwein<sup>15</sup> recommends a reagent containing 1.5-2.0 g. of methylene blue per liter of solution which is 4-6 N in hydrochloric acid. Losana<sup>16</sup> has used a method similar to that described above for the determination of titanium in siderurgical products. This method is not influenced by the presence of ferric chloride, manganous chloride, chromic sulfate, ammonium molybdate or sodium vanadate. Ferreri<sup>17</sup> has also used methylene blue for the determination of titanium in rocks and minerals.

**Determination of tin.** Stannous chloride, like titanous chloride, is oxidized quantitatively by methylene blue. Atack<sup>18-20</sup> has used this principle for the titrimetric determination of tin. A methylene blue hydrochloride solution which is free from methylene red is standardized in an atmosphere of carbon dioxide with standardized titanous chloride. The disappearance of the blue color gives an excellent end-point. The stannous chloride is then titrated with this standardized solution. The reagent is prepared and standardized by the method of Knecht,<sup>9</sup> or by reducing with titanous chloride solution, adding a portion of a potassium chlorate solution of known strength (about 0.7 g. per liter), and then reducing the methylene blue formed by titrating with titanous chloride. The value of the methylene blue solution is then determined in terms of oxygen of the potassium chlorate.

Leutwein<sup>15</sup> recommends titrating the stannous chloride solution with a reagent containing 1.5-2.0 g. of methylene blue in one liter 4-6 N hydrochloric acid. Two moles of  $C_{16}H_{18}N_3SCl$  equal 1 mole of  $SnCl_2$ . As a preliminary to

the tin determination, any stannic salts must be reduced to the stannous condition. According to Wohlmann,<sup>21</sup> reduction of stannic chloride is best effected in 15-20 per cent hydrochloric acid by means of zinc or aluminum. Iron is not suitable. If lead or antimony is present, aluminum must be used for the reduction, since otherwise tin is not deposited in a spongy condition. Methylene blue has been used to determine tin in alloys.<sup>64</sup>

**Detection and determination of chlorate.** Chlorates may be determined indirectly by the method described in the preceding section.<sup>18-20</sup> An excess of standardized stannous chloride is added to the chlorate solution, and the solution is then warmed in a current of carbon dioxide. When cold, an equal volume of hydrochloric acid is added and the excess stannous chloride titrated with methylene blue as described above.

When a 1 per cent solution of methylene blue is added to a 1 per cent solution of a chlorate, a precipitate consisting of dichroic, strongly doubly refracting prisms are formed. The dichroism is from blue to rose.<sup>22</sup>

**Detection and determination of molybdenum.** Molybdenum may be determined by a procedure based on the reduction of molybdenum by zinc and concentrated hydrochloric acid, and the subsequent oxidation of the reduced solution in an atmosphere of carbon dioxide with standardized methylene blue.<sup>23</sup> Molybdenum is reduced to molybdenum trichloride,  $\text{MoCl}_3$ , under these conditions, and the end-point of the reduction is indicated by an unusual shade of pink. The oxidation is accomplished by adding a solution of methylene blue containing 4 g. of the reagent per liter and standardized according to the method of Knecht.<sup>8,9</sup> During the oxidation, the pink color changes to green half way through the oxidation, and finally with an excess of 1 drop of the reagent the characteristic blue shade appears. The final product is molybdenum pentachloride,  $\text{MoCl}_5$ .

Monnier<sup>24</sup> has suggested the formation of a precipitate with an alkaline molybdate and methylene blue for the determination of molybdenum.

**Determination of phosphorus.** Quantities of phosphorus not exceeding 0.5 mg. may be determined titrimetrically with the aid of methylene blue. The yellow precipitate of ammonium phosphomolybdate is dissolved in ammonia and the molybdate reduced to the trivalent state with zinc and hydrochloric acid in the absence of oxygen. The reduced molybdenum is then oxidized with methylene blue as described in the preceding section. This method is unsatisfactory with larger quantities of molybdenum because of the formation of the blue reduction product of molybdenum.<sup>25</sup>

**Detection and determination of chromium, vanadium and iron.** Iron, chromium and vanadium may be determined by a procedure which is based upon the oxidation of leuco-methylene blue to methylene blue, and the subsequent determination of the latter with titanous chloride. In the reaction with the leuco derivative of methylene blue,  $\text{V}_2\text{O}_5$  is reduced to  $\text{V}_2\text{O}_4$ ;  $\text{CrO}_3$  is reduced to  $\text{Cr}_2\text{O}_3$ ; and  $\text{Fe}_2\text{O}_3$  is reduced to  $\text{FeO}$ . The oxidation is quantitative and the amount of vanadium, iron, or chromium can be estimated indirectly from the

amount of methylene blue formed in the reaction. Atack<sup>28</sup> gives the following directions for preparing the reagent and determining the metals:

**Reagent.** A known volume of standard methylene blue solution (about 4 g. of the dye per liter) is heated to boiling with dilute hydrochloric acid in a current of carbon dioxide, and then titrated while warm with titanous chloride solution until colorless. In this way the titanous chloride solution is standardized and leuco-methylene blue solution is obtained which is ready for the addition of the oxidizing agent which is to be determined. An excess of leuco-methylene blue must be present to prevent the formation of chlorine and the subsequent destruction of some of the methylene blue. Titrate in the presence of carbon dioxide at a temperature exceeding 40° C. in order to obtain a sharp end-point.

To determine chromium, convert the chromium salt to the chromate with the aid of sodium peroxide, and boil to destroy the excess sodium peroxide. Add an aliquot part of the solution so obtained to a solution of leuco-methylene blue prepared as described above. Then estimate the methylene blue so formed with the titanous chloride standardized as described above. Results obtained with this method are said to be excellent.

Vanadium may be estimated by a procedure identical with that described for chromium. Chromium and vanadium can be determined in the presence of iron, or all three can be determined together by a suitable modification of the above procedure.

Iron, chromium and vanadium may be detected by their ability to restore the original blue color of methylene blue in procedures similar to the above determination.

Methylene blue yields with dichromate a precipitate which may be used for the identification of chromium.<sup>24</sup>

**Detection and determination of perchlorate.** Perchlorate can be detected by a method which depends upon the formation of methylene blue perchlorate. With perchlorate, methylene blue forms a violet precipitate which when filtered and ignited decomposes without deflagration. This behavior makes possible the differentiation of perchlorate and persulfate, which also forms a violet precipitate with methylene blue.<sup>24</sup> The reaction is sufficiently sensitive to permit the detection of 0.003 mg. of perchlorate in a pure aqueous solution.<sup>27</sup> A solution of methylene blue containing a large quantity of zinc sulfate reacts with a nitrate solution containing perchlorate to give a color change from dark blue to greenish-blue and finally to reddish-violet. This reaction has been used by Hahn<sup>28</sup> for the detection and approximate determination of perchlorates in commercial nitrates.

Methylene blue reacts with perchlorate to give a violet precipitate which is soluble in hot water.<sup>29,30</sup> By treating a solution containing a perchlorate with a measured excess of standard methylene blue solution, a color is obtained which is inversely proportional to the quantity of perchlorate originally present. This inverse relation may be used for the colorimetric determination of perchlorates. By allowing the mixture to stand until the precipitate of methylene blue per-



chlorate has settled, the determination may be carried out by comparing the color of the supernatant liquid with that of standards.<sup>31</sup> By the addition of a large excess of zinc sulfate solution, precipitation can be prevented and the comparison can be made after 15 minutes.<sup>28</sup> The following method may be used for the determination of perchlorates in salts such as sodium nitrate.

**Procedure.** Dissolve 20 g. of the salt to be tested in water, and if iodides are present add a little moist silver oxide. Filter and dilute to 100 ml. Use a suitable aliquot, depending upon the perchlorate content. This is obtained as follows: For less than 0.2 per cent perchlorate use 10 ml. of the solution; for 0.2-0.5 per cent, use 5 ml. of the solution; and for a quantity greater than 0.5 per cent use 1 ml. Transfer the proper quantity of the solution to a test tube and dilute to 20 ml. Prepare a series of standards by adding quantities of 1 to 5 ml. of a 0.1 per cent solution of potassium perchlorate to tubes of the same size as those used for the unknown. To these standards, add the same volume of 20 per cent perchlorate-free solution of the same kind of salt that is being examined. In the analysis of Chili saltpeter, use pure sodium nitrate. Finally, dilute each standard to 20 ml.

To the unknown and to each of the standards, add 1 ml. of a 0.3 per cent aqueous solution of methylene blue. Allow the mixtures to stand for several hours in a cool place until precipitation occurs, and then compare the color of the sample with that of the series of standards.

Monnier's method for the determination of perchlorate by means of methylene blue may not give reliable results, since the precipitate which forms may carry down some nitrate. After washing the precipitate with a saturated solution of methylene blue perchlorate, the weight of the precipitate is proportional to the quantity of potassium perchlorate present, at least in quantities up to 0.3 per cent potassium perchlorate. For the colorimetric determination, washing with water is sufficient to eliminate the error.<sup>32</sup>

In a method proposed by Hahn,<sup>28</sup> zinc sulfate is used to prevent the precipitation of methylene blue perchlorate and thereby shorten the time required for the determination. Conditions used in Hahn's procedure vary somewhat depending upon the perchlorate content. The determination is carried out as follows:

**Procedure.** *Perchlorate exceeds 0.3 per cent:* Mix 5 ml. of a 0.032 per cent solution of methylene blue with 20 ml. of a 50 per cent solution of crystallized zinc sulfate. Add 0.2 ml. of the prepared sample solution and mix thoroughly. Allow to stand for 15 minutes and compare the resulting color with that of standards similarly prepared. The sensitivity is improved by comparison through a yellow glass filter.

*Perchlorate content from 0.05 to 0.3 per cent:* Mix 0.1 ml. of 1.6 per cent methylene blue solution with 25 ml. of 50 per cent crystallized zinc sulfate solution. Add 0.2 ml. of the sample solution and compare after 15 minutes with a series of standards similarly prepared.

*Perchlorate content less than 0.05 per cent:* Mix 0.1 ml. of 1.6 per cent methylene blue solution with 25 ml. of saturated zinc sulfate solution. Then

add 0.2 ml. of the sample solution and compare with a series of standards similarly prepared.

A special procedure is required for the determination of perchlorates in the presence of chlorates. For the analysis of chlorates containing perchlorate proceed as follows: <sup>33</sup>

**Reagent.** Mix 0.1 ml. of 1.6 per cent methylene blue solution with 25 ml. of 50 per cent crystallized zinc sulfate solution.

**Procedure.** To 0.2 ml. of the sample solution, or to 0.1 ml. of the sample solution and 0.1 ml. of water, add 0.1 ml. of 40 per cent potassium nitrate solution. Then add 5 ml. of the reagent and mix well. Compare with standards similarly prepared.

Prepare the standard solution by dissolving 0.1393 g. of potassium perchlorate in water and diluting to 1 liter. Dilute 100 ml. of this solution to 1 liter. One ml. of the diluted solution contains 0.01 mg. of the perchlorate radical.

Iodide interferes with the determination of perchlorate, but this can be removed with silver oxide. Fluoride, chloride, hypochlorite, chlorate, bromide, bromate, iodate, periodate, sulfate, nitrite, nitrate, phosphate, borate, perborate, carbonate and percarbonate do not interfere. Acid chromates interfere but may be precipitated by lead acetate in a neutral solution. Methylene blue also yields a precipitate in dilute acid solutions with permanganate, ferricyanide, vanadate, molybdate and tungstate. More than 5 per cent of sodium nitrate or 10 per cent of potassium nitrate interferes by precipitating some of the methylene blue. <sup>34</sup>

**Detection of peroxides and persalts.** Leuco-methylene blue, prepared by the action of sodium thiosulfate on methylene blue in an aqueous hydrochloric acid solution, may be used for the detection of peroxides and persalts: <sup>35</sup>

**Reagent.** To 10 ml. of a 0.1 per cent aqueous solution of methylene blue, add 10 drops of 12 per cent sodium thiosulfate solution and 20 drops of 1 per cent hydrochloric acid. Mix thoroughly and allow to stand 5-15 minutes until the solution is perfectly colorless. This solution is stable for about 12 hours.

**Procedure.** Place about 0.5 ml. of the reagent and 0.5 ml. of ether in a small tube and carefully pour 2-3 drops of the solution to be tested down the inclined wall of the tube so that it passes through the ether layer and spreads out at the surface of the reagent. In the presence of peroxide or persalts, a blue ring soon forms. The intensity of the color is proportioned to the quantity of active oxygen present.

Persulfate, permanganate, dichromate, vanadate and molybdate may be detected by the colored precipitate which they form with methylene blue.

The precipitation of methylene blue permanganate has been suggested as a test for the permanganate ion, <sup>36,37</sup> but this reaction is not recommended, since it is given by many ions. <sup>38</sup>

**Detection of copper, mercury, silver and tin.** The leuco derivative of methylene blue can be used for the detection of many substances which are

easily reduced.<sup>39, 63</sup> This reaction may be used for the detection of some cations such as stannic tin, mercuric mercury, and cupric copper. The leuco-base of methylene blue is prepared as follows:

**Preparation:** To 10 ml. of a 0.1 per cent aqueous solution of methylene blue, add 10 drops of 12 per cent sodium thiosulfate solution and 20 drops of 1 per cent hydrochloric acid. Stir to insure thorough mixing and allow to stand for 5-15 minutes until the solution is perfectly colorless. This solution is stable in air for about 12 hours and can be used as a test reagent, or a test paper can be prepared with it.

Oxidizing substances, including oxidizing cations cause this solution to turn blue.

A solution of  $K_2HgI_4$ , which is prepared by saturating a concentrated solution of potassium iodide with mercuric iodide, reacts with methylene blue to form an insoluble compound. If a suspension of the insoluble methylene blue iodo-mercurate is added to a solution containing a silver salt, silver iodide is precipitated, and the solution turns blue, due to the liberation of methylene blue. From the depth of color so formed, the amount of silver present can be estimated. This reaction is useful, not only for the determination of silver, but also for the indirect determination of various anions, such as the halides, which are precipitated with silver ions. The test with methylene blue iodo-mercurate is obtained only after an excess of silver has been added. Mercuric ions react similarly, but the color produced is not exactly proportional to the mercuric ion concentration as it is with silver ions. Sulfides interfere with this test, but very few other ions except those which are colored affect the test. The reaction is sensitive to 1 $\gamma$  of silver.<sup>40</sup>

Kul'berg<sup>41</sup> has prepared an iodo derivative of methylene blue of unknown composition, which can be used as a very sensitive reagent for silver, mercury and tin. The reagent is prepared as follows:

**Reagent.** Add an excess of a 0.1 N solution of iodine in potassium iodide to a 1 per cent aqueous solution of methylene blue. Stir the mixture and allow to stand overnight. Filter and wash, first with the potassium iodide solution, and then with 0.01 per cent sulfuric acid.

**Procedure.** Place a drop of the reagent solution on a strip of filter paper, and then add a drop of a moderately acid solution to be tested. A blue coloration appears if silver, mercury or tin is present. This reaction serves to detect 0.002 $\gamma$  of silver, 0.021 $\gamma$  of mercury and 0.6 $\gamma$  of tin.

The iodo derivative of methylene blue may also be used for a very sensitive test for sulfide, sulfite and thiosulfate.

**Detection of cerium.** The red color which is formed when methylene blue is added to an acid solution of a ceric salt was observed by Passerini and Michelotti,<sup>42</sup> who have recommended the reaction as a test for ceric cerium. The color is transitory, and better results are obtained by the use of an alkaline solution. Trivalent cerium does not give the reaction, and must be oxidized with potassium permanganate. The reaction takes place at room temperature,

and in neutral or slightly acid solutions, except in the presence of vanadium salts in which case the medium should be slightly alkaline. The following test is recommended by Reed:<sup>43</sup>

**Procedure.** To 50 ml. of an aqueous solution to be tested in a Nessler tube, add dropwise 5 N sulfuric acid until the solution is distinctly acid. Then add a drop of hydrogen peroxide solution and a drop of 0.5 per cent methylene blue solution. Shake and add 5 N sodium hydroxide until the mixture is alkaline. A blue color is obtained with as little as 1 part of cerium in 1,000,000 parts of solution.

This reaction is not quantitative and cannot be used for the colorimetric determination of cerium.<sup>43</sup>

Wenger and co-workers<sup>44</sup> have studied the use of methylene blue for the detection of cerium and claim that it is not sufficiently sensitive to be of great value.

**Detection of rhenium.** Methylene blue yields characteristic blue needles of methylene blue perrhenate. This reaction has been used for the microchemical detection of rhenium.<sup>45-47</sup> This reaction, however, does not appear to be sufficiently sensitive nor specific to be of great value.<sup>48</sup>

**Detection of tantalum.** Methylene blue yields with tantalum a fine-grained, grayish-blue precipitate which may be used for the detection of as little as 1 $\gamma$  of tantalum. A 0.1 per cent aqueous solution of methylene blue is used as the reagent. Tungsten, molybdenum, vanadium, antimony, tin and aluminum may interfere.<sup>49</sup>

**Detection of cobalt.** Dwyer<sup>50</sup> recommends the following test for cobalt:

**Procedure.** Add a dilute solution of potassium permanganate to 5-10 ml. of a hot acid solution of a cobalt salt until a permanent pink color is obtained. Decolorize the solution with a few drops of sulfurous acid, and then add 5-10 drops in excess. Add 5-10 drops of potassium thiocyanate solution and boil until any red color due to ferric thiocyanate is discharged and any copper present is precipitated as cuprous thiocyanate. Now add a little 0.05 per cent methylene blue solution and an excess of 1 per cent sodium sulfite in 2 N potassium cyanide solution. If cobalt is present, the blue color fades but reappears on standing in air or upon shaking.

Cobalt can be confirmed in the filtrate obtained after precipitating nickel with dimethylglyoxime as follows: Acidify the filtrate, boil with 2 drops of sulfurous acid reagent and a little methylene blue, and then make alkaline with ammonium hydroxide. A decolorization with the subsequent return of the color indicates cobalt.

**Determination of calcium, magnesium and potassium.** Bolliger<sup>51,52</sup> has used methylene blue for the titrimetric determination of picric and picrolonic acids and picrates and picrolonates. This principle has been used for the indirect titrimetric determination of calcium, magnesium and potassium. For the deter-

mination of calcium, the cation is precipitated from a neutral or slightly acid solution with a known excess of a standard lithium picrolonate solution, and the filtered excess of the picrolonate is determined by titration with methylene blue.<sup>53</sup>

The following method may be used for the determination of calcium in biological materials:<sup>54,55</sup>

**Procedure.** First determine the approximate calcium content of the sample by a preliminary test, and add a quantity of buffer containing 1 M acetic acid, 0.125 M lithium acetate and 1 M lithium chloride ( $\text{pH} = 3.6\text{--}3.8$ ) so that it will be diluted ten-fold in the final mixture. Then to 5 or 10 ml. of the unknown add such quantity of standardized 0.01 M picrolonic acid that after complete precipitation the concentration of the acid will be at least 0.001 M. The amount of picrolonic acid added should not exceed 4 times the molar concentration of calcium. Keep the mixture in ice overnight if the calcium concentration is less than 0.005 M. If the calcium concentration is greater than this, allow to stand at a temperature not exceeding  $20^{\circ}\text{C}$ . Filter through a Jena G4 sintered glass crucible. Bring the filtrate to room temperature, and titrate an aliquot as follows:

Transfer an aliquot of the filtrate, which should correspond to 2-10 ml. of 0.001-0.005 M picrolonic acid, to a separatory funnel and add 20-30 ml. of chloroform and 2 ml. of an acetate or phosphate buffer of  $\text{pH}$  4-8. Titrate with 0.001 M methylene blue chloride. Determine the approximate concentration of the picrolonic acid by a preliminary titration, and then to a second aliquot add a quantity of methylene blue chloride which is 1-2 ml. less than that required for the complete titration. Extract the methylene blue picrolonate with 20-ml. portions of chloroform until a freshly added portion remains colorless. Complete the titration by successive additions of about 0.15 ml. of the methylene blue chloride solution, and extract each time the blue-green product with 20-ml. portions of chloroform. The end-point is reached when the chloroform fails to remove the blue color from the solution.

The methylene blue solution is standardized in the same way with picrolonic acid solutions of known strength. Magnesium is determined in a similar manner.<sup>56</sup> For the details of this determination, see section on picrolonic acid.

Since picric acid can be determined titrimetrically by titration with methylene blue,<sup>51</sup> potassium can be determined indirectly by precipitating as potassium picrate and determining the picric acid content of the precipitate with the aid of methylene blue.<sup>57-59</sup> For the details of this procedure, see section on picric acid.

Bolliger<sup>59</sup> has described an indirect method for the titration of potassium which is based upon the titration of perchloric acid with methylene blue. Potassium is precipitated as the perchlorate, and the precipitate is dissolved in water and treated with a measured volume of standard methylene blue chloride solution. The resulting precipitate of methylene blue perchlorate is filtered off and the excess methylene blue titrated with the aid of a solution of picric acid. The fact that methylene blue perchlorate or picrate can be extracted with chloroform,

although both methylene blue and picric acid are insoluble in this solvent, permits a sharp recognition of the end-point of the titration. This procedure may also be used for the titrimetric determination of perchloric acid or perchlorates. For details of the titration, see section on picric acid.

**Reactions of metals with methylene blue.** Passerini and Michelotti<sup>42</sup> have studied the reactions of methylene blue with many metal salts and report their results in Tables 62 and 63.

**Detection and determination of oxygen.** Rienisdijk<sup>60</sup> has used methylene blue in a reagent for the detection of oxygen:

**Reagent.** Mix 3 ml. of a 10 per cent glucose solution, 1 drop of N sodium hydroxide solution, and 1 drop of a 0.1 per cent solution of methylene blue.

**Procedure.** Immerse folded strips of gauze in the reagent and insert into a vessel containing oxygen. The reagent is decolorized in 1 minute at a temperature of 37° C.

Kling and Clariz<sup>61</sup> have used methylene blue for the determination of oxygen in gases. The method depends upon the fact that an alkaline solution of a ferrous salt absorbs oxygen, and that if a little methylene blue is present, the solution, colorless at first, becomes blue in the presence of oxygen. From the volume of a gaseous mixture required to cause this change in color the per cent of oxygen can be calculated.

**Detection of cyanide.** A 1 per cent solution of silver nitrate which is slightly colored with methylene blue produces blue crystals of silver cyanide when added to plant material containing cyanides.<sup>62</sup>

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TABLE 62.—REACTIONS OF METALS WITH METHYLENE BLUE

Salt	Medium	Remarks
AgNO <sub>3</sub>	Neutral	No reaction
HgNO <sub>3</sub>	Neutral	No reaction
Tl <sub>2</sub> SO <sub>4</sub>	Neutral or sulfuric acid	No reaction
Cu(NO <sub>3</sub> ) <sub>2</sub>	Neutral or sulfuric acid	No reaction
Pb(NO <sub>3</sub> ) <sub>2</sub>	Nitric acid	No reaction
PbCl <sub>2</sub>	Hydrochloric acid	No reaction
Bi(NO <sub>3</sub> ) <sub>3</sub>	Nitric acid	No reaction
Cd(NO <sub>3</sub> ) <sub>2</sub>	Nitric acid	No reaction
Na <sub>3</sub> AsO <sub>4</sub>	Neutral	No reaction
Na <sub>3</sub> AsO <sub>3</sub>	Neutral	No reaction
SbCl <sub>3</sub>	Hydrochloric acid	No reaction
Sb <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	Sulfuric acid	No reaction
FeCl <sub>2</sub>	Neutral	No reaction
FeCl <sub>3</sub>	Neutral	No reaction
AlCl <sub>3</sub>	Neutral	No reaction
Cr <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	Neutral	No reaction
UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	Neutral	No reaction
Zr(NO <sub>3</sub> ) <sub>4</sub>	Neutral	No reaction
Be(NO <sub>3</sub> ) <sub>2</sub>	Neutral	No reaction
Th(NO <sub>3</sub> ) <sub>4</sub>	Neutral	No reaction
NiSO <sub>4</sub>	Neutral or sulfuric acid	No reaction
NiCl <sub>2</sub>	Neutral or sulfuric acid	No reaction
CoSO <sub>4</sub>	Neutral or sulfuric acid	No reaction
CoCl <sub>2</sub>	Neutral or sulfuric acid	No reaction
Ca(NO <sub>3</sub> ) <sub>2</sub>	Neutral	No reaction
Ca(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub>	Neutral	No reaction
Ba(NO <sub>3</sub> ) <sub>2</sub>	Neutral	No reaction
Ba(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub>	Neutral	No reaction
Sr(NO <sub>3</sub> ) <sub>2</sub>	Neutral	No reaction
Sr(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub>	Neutral	No reaction
MgCl <sub>2</sub>	Neutral	No reaction
NH <sub>4</sub> Cl	Neutral	No reaction
CdCl <sub>2</sub>	Hydrochloric acid	Blue precipitate after 12 hours
SnCl <sub>4</sub>	Neutral	Violet precipitate after 24 hours
FeSO <sub>4</sub>	Neutral	Brown red precipitate
MnCl <sub>2</sub>	Neutral	Colorless precipitate
ZnCl <sub>2</sub>	Neutral	Blue precipitate
NaCl	Neutral	Slightly colorless precipitate
LiCl	Neutral	Slightly colorless precipitate
KCl	Neutral	Slightly colorless precipitate
Ti(NO <sub>3</sub> ) <sub>4</sub>	Nitric acid	Blue precipitate
Ti(SO <sub>4</sub> ) <sub>3</sub>	Sulfuric acid	Blue precipitate
NaVO <sub>3</sub>	Neutral or alkaline with sodium hydroxide	Immediate blue precipitate
(NH <sub>4</sub> ) <sub>2</sub> WO <sub>4</sub>	Neutral	Immediate blue precipitate
SnCl <sub>2</sub>		Decolorizes reagent

TABLE 63.—REACTIONS WITH INORGANIC SALTS OF METHYLENE BLUE

Salt	Medium	Color	Composition	Color immediate but no precipitate
$\text{Ce}(\text{SO}_4)_2$	Neutral or $\text{H}_2\text{SO}_4$	Scarlet	$[\text{C}_{10}\text{H}_{18}\text{N}_3\text{SCl} \cdot \text{Ce}(\text{SO}_4)_2]$	Color immediate but no precipitate
$\text{HgCl}_2$	Neutral or $\text{H}_2\text{SO}_4$	Violet-red	$[\text{C}_{10}\text{H}_{18}\text{N}_3\text{SCl} \cdot \text{HgCl}_2]$	Immediate precipitate
$\text{IrCl}_3$	Neutral or acid by $\text{HCl}$	Blue	$[\text{C}_{10}\text{H}_{18}\text{N}_3\text{SCl} \cdot \text{IrCl}_3]$	Immediate precipitate
$\text{PdCl}_2$	Neutral or acid by $\text{HCl}$	Dark green	$[\text{C}_{10}\text{H}_{18}\text{N}_3\text{SCl} \cdot \text{PdCl}_2]$	Immediate blue-violet precipitate which turns green
$\text{AuCl}_3$	Neutral or acid by $\text{HCl}$	Dark green	$[\text{C}_{10}\text{H}_{18}\text{N}_3\text{SCl} \cdot \text{AuCl}_3]$	Immediate precipitate
$\text{H}_2\text{PtCl}_6$	Acid by $\text{HCl}$	Violet-blue	$[\text{C}_{10}\text{H}_{18}\text{N}_3\text{SCl} \cdot \text{H}_2\text{PtCl}_6]$	Immediate precipitate
$\text{MoO}_2\text{Cl}_2$	Acid by $\text{HCl}$	Violet-blue	[Composition containing 79.56 per cent of $\text{H}_2\text{MoO}_4$ ]	Immediate precipitate
$(\text{NH}_4)_2\text{MoO}_4$	Acid by $\text{HNO}_3$	Violet-blue	[Composition containing 79.56 per cent of $\text{H}_2\text{MoO}_4$ ]	Immediate precipitate
$\text{K}_2\text{Cr}_2\text{O}_7$	Neutral	Brown-red	$[\text{C}_{10}\text{H}_{18}\text{N}_3\text{SCl} \cdot \text{K}_2\text{Cr}_2\text{O}_7]$	Immediate precipitate
$\text{KSCN}$	Neutral	Green	$[\text{C}_{10}\text{H}_{18}\text{N}_3\text{S} \cdot \text{SCN}]$	Immediate violet precipitate which turns green
$\text{K}_3\text{Fe}(\text{CN})_6$	Neutral	Dark green	$[\text{C}_{10}\text{H}_{18}\text{N}_3\text{SCl} \cdot \text{K}_3\text{Fe}(\text{CN})_6]$	Immediate precipitate
$\text{K}_4\text{Fe}(\text{CN})_6$	Neutral	Dark blue	[Composition containing 20 per cent $\text{K}_4\text{Fe}(\text{CN})_6$ ]	Slow forming precipitate

All precipitates are soluble in dilute mineral acids and in excess water. Reactions are uncertain below 0.5 per cent solutions because of decomposition of colored products, except with cerium, in which case reaction is well defined within 0.005 per cent solutions.



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## METHYL GREEN

$C_{26}H_{33}N_3Cl_2 \cdot ZnCl_2$

Mol. Wt. 594.74

Color Index, 684.

**Use:** Detection of ferricyanide.

Methyl green consists of small green crystals which possess a golden luster. The dye dissolves in water to yield a bluish-green solution.

**Preparation:** Methyl green is prepared by the action of methyl chloride on an amyl alcohol solution of methyl violet, which is kept neutral by the gradual addition of sodium hydroxide.

**Detection of ferricyanide.** Lapin<sup>1</sup> has studied the use of a number of leuco derivatives of di- and triphenylmethane dyes as reagents for the ferricyanide ion in restoring the color of the dye. Methyl green is claimed to be one of the most satisfactory reagents.

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## METHYL ORANGE

Synonym: Helianthin, orange III, gold orange, tropaeolin D,  
sodium *p*-dimethylaminoazobenzenesulfonate

$C_{14}H_{14}O_3N_3SNa$

Mol. Wt. 327.33

Beil. Ref. XVI, 331.



**Use:** Detection of bromate, calcium, cerium, chlorine, cobalt, cyanide, hypochlorite, magnesium, manganese and nickel.

Determination of boron, chlorine, copper, tin, titanium and water.

Methyl orange consists of an orange-yellow powder or crystalline scales. It is soluble in 500 parts of cold water, more soluble in hot water, and practically insoluble in alcohol.

**Preparation:** Dissolve 20 g. of sulfanilic acid in 50 ml. of 2 N sodium hydroxide solution, and add 8 g. of sodium nitrite dissolved in 100 ml. of water. Cool the mixture in ice, and pour into 50 ml. of cold 2 N hydrochloric acid. Mix this solution with a previously prepared mixture of 12 g. of dimethylaniline in 100 ml. of N hydrochloric acid, and make the mixture distinctly alkaline with sodium hydroxide. Allow to stand for several hours and filter as dry as possible with suction. Purify by recrystallizing from a little water.

**Detection of metals.** The acid obtained from methyl orange has been used by Pozzi-Escot<sup>1-4,16</sup> for the microdetection of a number of metals. Mercury, gold, copper, palladium, lead, tin, silver, cadmium, zinc, chromium, thorium, uranium, cobalt, nickel, lanthanum, manganese, iron, beryllium, cerium, strontium, calcium, magnesium, lithium, aluminum, rubidium, neodymium and praseodymium form crystals which in most cases are well-formed and adaptable to the microdetection of these elements. Cobalt and nickel are particularly easily distinguished.

The crystals formed with cobalt are large prismatic needles of a violet or black color, and these may be obtained in the presence of a large quantity of nickel salts. The nickel compound consists of yellow-green amorphous needles, which dissolve in water and then separate as pale yellow glistening crystals. Lead yields yellow hexagonal crystals; stannous tin, orange yellow crystals; chromium, orange-yellow crystals; uranium, yellow crystals; cerium, long black needles; and aluminum, dark violet crystals. Magnesium gives a reaction similar to that of nickel, but the crystals are of different character and smaller than those of nickel. Calcium is precipitated as prismatic needles in a very sensitive reaction.

**Determination of tin.** Small quantities of tin can be determined by a titrimetric procedure which is based upon the reduction and decomposition of methyl orange by tin in an acid solution to form sulfanilic acid and dimethyl-*p*-phenylenediamine. The following procedure has been used by Alimarin and Pevzner<sup>5</sup> for the determination of small amounts of tin in ores:

**Procedure.** Fuse 3-5 g. of the ore with 18-30 g. of sodium peroxide. Shake the melt with water and dilute the suspension to 500 ml. Allow the mixture to settle. Acidify 300-400 ml. of the clear supernatant liquid with hydrochloric acid to about 3 N, add 2-3 g. of tartaric acid and 2-3 g. of boric acid, and treat with hydrogen sulfide for 30-40 minutes. Filter, wash with 3 per cent aqueous ammonium chloride saturated with hydrogen sulfide, and dissolve the precipitate in sulfuric acid. Add 60 ml. hydrochloric acid ( $d = 1.2$ ) and add 50 ml. of water. Boil with an excess of lead foil for one hour in an atmosphere of carbon dioxide, which is free from hydrogen sulfide and oxygen.

Finally, titrate with a 0.01 or 0.05 per cent solution of methyl orange in water from which all air has been expelled. The solution of methyl orange is standardized against a standard solution of tin.

Trivalent antimony, arsenic, bismuth, and divalent copper, cadmium, lead, and iron, and salts of the alkali metals change the color of the methyl orange solution somewhat, but this does not affect the accuracy of the tin determination. Titanium, vanadium, molybdenum and tungsten in the lowest oxidation state also decolorize the methyl orange solution and must be removed before making the tin determination. The accuracy of this method is about the same as that of the iodometric determination, but it possesses the advantage that the titration may be repeated on the same sample by the simple process of reducing the tin in the solution.

**Determination of titanium.** Gautier<sup>6,7</sup> recommends the use of methyl orange for the preparation of a permanent standard comparison scale to be used in the colorimetric determination of titanium by the hydrogen peroxide method. The solutions do not fade and are easily prepared. The standards are prepared as follows:

**Procedure.** Dissolve 1 g. of methyl orange in 500 ml. of water and dilute 10 ml. of this solution to 200 ml. Using small volumes of this solution, prepare a series in which the color intensity is made to vary over the desired range. Standardize these solutions against a standard titanium solution which has been oxidized by means of hydrogen peroxide. Keep solutions stoppered when not in use to prevent the change in color due to evaporation.

**Determination of copper.** Methyl orange has been proposed as a color standard in the determination of copper with benzidine.<sup>16</sup> For details, see section on benzidine.

**Determination of boron.** Methyl orange has been used for the preparation of color standards to be used in the alizarinsulfonic acid method for the colorimetric determination of boron in plant material.<sup>8</sup>

**Procedure.** Ash 0.5-1.0 g. of the material to be analyzed in a porcelain crucible at 480-525° C. Add exactly 5 ml. of 0.4 N sulfuric acid and triturate the mixture with a rubber-tipped stirring rod. Allow the residue to settle, and pipet off 1 ml. of the clear supernatant liquid into a special test tube. Add 9 ml. of a solution containing 0.01 g. of alizarinsulfonic acid, mix, cool if necessary, allow to stand for 30 minutes, and compare the resulting color with that of a series of methyl orange standards.

The standards are prepared by dissolving 0.1 g. of methyl orange in 100 ml. of 95 per cent ethyl alcohol and 100 ml. of water. This solution is standardized as follows: prepare a series of dilutions of boric acid containing up to 0.005 mg. of boron per liter, and then mix with 9 ml. of a solution containing 0.01 g. of alizarinsulfonic acid. Allow the mixture to stand for 30 minutes for the color to develop, and then run the methyl orange solution into an exactly similar tube until the colors match when viewed vertically.

**Detection and determination of chlorine.** Free chlorine and hypochlorites in an acid solution can be detected by means of methyl orange.<sup>9,17</sup> If chlorine water or a solution of hypochlorite is made alkaline and then treated with methyl orange, the mixture is yellow in color; but upon acidifying the solution, the color is bleached.

The chlorine test is carried out as follows:

**Procedure.** To 250 ml. of the water to be tested, and to an equal quantity of distilled water, add 1-2 drops of a 1:5000 solution of methyl orange and 2-3 ml. of hydrochloric acid. The color disappears if free chlorine or a hypochlorite is present, while the blank remains rose-red. As little as 0.1 mg. of chlorine per liter can be detected. The test is more sensitive with methyl red.

Winkler<sup>10</sup> has based a method for the determination of active chlorine in water upon the decolorization of a methyl red or methyl orange solution by free chlorine. Korenmann<sup>11</sup> suggests substituting methyl orange for methyl red for the determination of from 0.04-7.9 mg. of chlorine per liter. The results obtained with this reagent agree within less than 4 per cent with values obtained by the microiodometric method, but it is necessary to standardize the methyl orange solution against a solution of known chlorine content. The procedure consists simply in titrating with a methyl orange solution containing 0.33 g. of the dye in a liter of solution to the first appearance of color.

**Detection of manganese.** A modification of Winkler's chlorine test with methyl orange<sup>10,17</sup> can be used for the detection of manganese in water:<sup>17</sup>

**Procedure.** To each of two 250-ml. portions of water add 1 drop of 1:5000 methyl orange. To the first portion add 1-2 ml. of 10 per cent sodium hydroxide and allow to stand a few minutes. Then to both portions add 5 ml. of 10 per cent hydrochloric acid. If manganese is present, the first portion is decolorized after 1-2 minutes. The test is sensitive to 0.1 mg. of manganese per liter.

Iron does not interfere, but nitrite and much organic matter diminishes the sensitivity of the test. In the presence of hydrogen sulfide, the method is unreliable.

**Detection of bromate.** Bromates can be detected by the following procedure employing methyl orange:<sup>12</sup>

**Procedure.** Add 1 ml. of 3-4 N hydrochloric acid and 1-2 drops of 0.015 per cent methyl orange solution to 2 ml. of the solution to be tested. The solution is immediately decolorized if bromate is present. By this reaction 14 $\gamma$  of potassium bromate can be detected in 2 ml. of solution.

The reaction is satisfactory even in the presence of potassium chlorate, potassium iodate, ammonium persulfate and other oxidizing agents, since under the conditions of the test several minutes are required for these substances to decolorize the methyl orange.

**Detection of hydrogen cyanide.** Sherrard<sup>13</sup> has proposed the use of methyl orange as a reagent for the convenient and rapid detection of hydrogen cyanide gas in enclosures after fumigation. The test depends upon the change of color of Whatman No. 40 filter paper which has been immersed in a mixture of methyl orange and mercuric chloride solutions to which glycerol has been added, and then allowed to dry. The reagent paper is orange in color, but this changes to pink upon exposure to hydrogen cyanide gas.

**Reagents.** *Mercuric chloride solution:* Dissolve 1.25 g. of mercuric chloride in 250 ml. of distilled water.

*Methyl orange solution:* Dissolve 0.6 g. of methyl orange in 250 ml. of distilled water.

Mix 10 ml. of the mercuric chloride solution and 5 ml. of the methyl orange solution and then add 1 ml. of glycerol. Impregnate Whatman No. 40 filter paper with this solution and suspend in acid-free air until dry. Cut into strips one quarter inch wide, and preserve in a glass tube. Protect from light.

**Procedure.** To test for hydrogen cyanide, simply expose the paper to air suspected of containing the gas for about two minutes. A 10 per cent error in the time of exposure does not materially affect the test, which is the appearance of a slight pink color. Do not use in air containing much moisture, such as during a rain or in a heavy fog.

The sensitivity of this reaction is not as great as that of other procedures for cyanides, but it is sensitive to less than the lethal quantity, and hence is satisfactory for detecting hydrogen cyanide vapors in rooms or ships that have been fumigated with this gas. The benzidine-copper acetate test is too sensitive and too rapid for practical use.

**Determination of water.** Kolthoff<sup>14</sup> has used methyl orange for the colorimetric determination of the water content of so-called absolute alcohol. The method is based upon the fact that the sensitivity of certain azo-indicators such as methyl orange to acid decreases with increased ethyl alcohol concentration of the medium.

**Procedure.** Place 25 ml. of water in a Nessler tube, and add 0.1 ml. of a saturated solution of methyl orange in ethyl alcohol and 0.4 ml. of 0.01 N aqueous hydrochloric acid. The intermediate orange red color of methyl orange is obtained. In a second Nessler tube place 25 ml. of the ethyl alcohol to be analyzed, and add 0.12 ml. of a saturated alcoholic solution of methyl orange, and then add a 0.1 N hydrochloric solution in ethyl alcohol (prepared by passing dry hydrogen gas into ethyl alcohol) from a Bang buret until the color is the same as that in the first tube. Observe the temperature of the alcohol solution. For temperatures above 15° C. and concentrations ranging from 95.0 to 99.7 per cent, interpolations may be made by reference to Table 64, which has been prepared by Kolthoff:

TABLE 64.

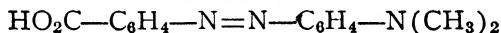
Alcohol Volume Per Cent	0.1 N Alcoholic HCl to Match Color of Aqueous Solution ml.	Correction for Each Degree Above 15
99.7	0.21	0.007
99.0	0.96	0.03
98.0	2.27	0.07
97.0	3.45	0.10
96.0	4.30	0.12
95.0	5.05	0.13

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**METHYL RED**Synonym: Dimethylaminoazobenzene-*o*-carboxylic acid $C_{15}H_{15}N_3O_2$ 

Beil. Ref. XVI, 329 (315). Color Index, 211.

Mol. Wt. 269.29

**Use:** Detection of chlorine and nitrite.**Determination of chlorine.**

Methyl red consists of lustrous violet crystals or a dark red powder. It is slightly soluble in water, but is soluble in alcohol and glacial acetic acid. The sodium salt is soluble in water.

**Preparation:** Mix 137 g. of anthranilic acid, 1 liter water, 300 g. of crushed ice, and 222 ml. of hydrochloric acid ( $d = 1.18$ ), and diazotize with a solution of 59 g. of sodium nitrite in 150 ml. of water which has been cooled to below 5° C. Stir for 20 minutes, and add to a mixture of 121 g. of dimethylaniline and 200 ml. of water, and then add 90 ml. of hydrochloric acid ( $d = 1.15$ ). Allow to stand for a few minutes, and add a mixture of 165 g. of fused sodium acetate and 50 ml. of water. Purple-red crystals of the dye separate from the solution after a few hours.<sup>1</sup>

**Detection and determination of chlorine.** Winkler<sup>2,4</sup> has used a solution of methyl red for the detection and determination of free chlorine. This reaction is based upon the fact that methyl red is decolorized by a solution containing free chlorine. This test is sensitive to 0.02 mg. of chlorine in 500 ml. of water.<sup>4</sup> This procedure may be made quantitative by titrating an unknown chlorine solution with a standard solution of methyl red to the appearance of a faint pink color.

**Reagent.** Dissolve 0.1 g. of methyl red in 10 ml. of N sodium hydroxide and dilute this solution to 1 liter with boiled, distilled water. One ml. of this solution is equivalent to 0.05 mg. of free chlorine.

**Procedure.** Acidify 100 ml. of water to be analyzed with 1 ml. of dilute hydrochloric acid, and then add the methyl red reagent from a buret until the liquid is pale red in color. Winkler recommends that the first determination be used as a preliminary, and that a second determination be made by adding to 100 ml. of water, which is not acidified with hydrochloric acid, the quantity of the reagent solution determined in the first titration; and then, after acidifying the mixture with 1 ml. of hydrochloric acid, completing the titration by the dropwise addition of the reagent to a faint red end-point. Divide the number of ml. of reagent solution required in the titration by two to obtain the quantity of free chlorine present in mg. of chlorine per liter of solution.

According to Korenman<sup>3</sup> the results obtained by using this method do not agree with those obtained by the microiodometric procedure unless the methyl red solution is standardized against a solution containing a known quantity of active chlorine.

**Detection of nitrite.** Nitrites may be detected by a reaction based upon the fact that in a warm acid medium they destroy such indicators as methyl red and methyl orange. The following method is used for the detection of nitrite in water:

**Procedure.** To 100 ml. of the water to be tested, add 1 ml. of a solution containing 10 mg. of methyl red per liter, and acidify with hydrochloric acid. Heat the mixture over a wire screen. The color is completely decolorized if the nitrite concentration is 0.1 mg. of  $N_2O_3$  per liter. If the solution is even partially decolorized, less than 0.03 mg. of nitrite nitrogen is indicated.

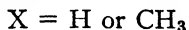
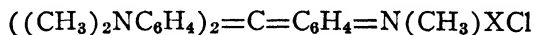
Free chlorine and bromine interfere, since they also decolorize the reagent. Ferric iron also interferes, but this may be eliminated by the addition of sodium fluoride. Manganous salts and ferrous salts in concentrations up to 5 mg. per liter do not interfere. Nitrate in concentrations exceeding 50 mg. of nitrogen per liter reacts like nitrite, but at lower concentration nitrate decolorizes methyl red only after prolonged heating.

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3. I. M. Korenman, *Mikrochemie.* **19**, 144-6 (1936); *C.A.* **30**, 4428 (1936).
4. L. W. Winkler, *Z. angew. Chem.* **28**, 22-3 (1915); *C.A.* **9**, 1517 (1915).

## METHYL VIOLET

Synonym: Methylrosaniline, crystal violet, aniline violet, methylrosaniline chloride, gentian violet

Color Index, 680.



**Use:** Detection of tantalum and zinc.

Methyl violet is a mixture of the penta- and hexamethyl *p*-rosaniline chlorides. The commercial dye usually consists of one part dextrin with one part of the



dye, and also a little tetramethyl-*p*-rosaniline. The dye consists of a dark green powder which has metallic luster. It is soluble in water, alcohol and chloroform, but is insoluble in ether.

**Detection of tantalum.** A 0.1 per cent aqueous solution of methyl violet gives coarse violet flakes when added to a solution containing tantalum. The reaction is sensitive to 0.04% of the metal. Alkali salts of tungsten, vanadium, columbium and tin interfere.<sup>1</sup>

**Detection of zinc.** Zinc may be detected by a procedure employing methyl violet.<sup>2</sup>

**Procedure.** To 2 ml. of the neutral solution to be tested, add 1 drop of hydrochloric acid ( $d = 1.12$ ), 1 drop of 0.06 per cent solution of methyl violet, and 2 drops of 20 per cent ammonium thiocyanate solution. If zinc is present, a blue or violet color appears when the solution is viewed by transmitted light. In the absence of zinc, a bluish-green color is observed. The addition of 5 drops of a saturated solution of tartaric acid prevents interference by elements other than gold, platinum, and palladium. The sensitiveness of this reaction is 1:15,000,000. One part of zinc can be detected in the presence of 10,000 parts of cadmium.

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### $\beta$ -NAPHTHYLIMINO-8-DINAPHTHOXAZINE

$C_{30}H_{18}N_2O$

Mol. Wt. 422.44

**Use:** Detection of nitric acid.

This dye is a brown solid. It is insoluble in water, methyl alcohol and ethyl alcohol, but it is soluble in alcoholic hydrogen chloride and sulfuric acid with violet solutions.

**Preparation:** Mix 10 g. of phenylamino-1-hydroxy-2-naphthalene, 50 g. of  $\beta$ -naphthylamine, 4 g. of hydrated copper oxide and 100 ml. of pyridine, and agitate for 10 hours at room temperature in the presence of air. Replace the pyridine which evaporates to keep the naphthylamine in solution, and allow the mixture to stand overnight. Filter the brown precipitate. Distill the greater part of the pyridine, and add about 300 ml. of alcohol to the residue. Cool, and filter off an additional quantity of the brown precipitate and combine with the first. Crystallize from xylene and wash with methyl alcohol.<sup>1,2</sup>

**Detection of nitric acid.** Lantz<sup>1-3</sup> has shown that dissymmetrical arylimino-8-dinaphthoxazines dissolved in concentrated sulfuric acid turn violet when treated with small quantities of nitric acid. A solution containing 0.2 g. of the oxazine in 1000 g. of 93 per cent sulfuric acid is a satisfactory reagent. As

little as 50 mg. of nitric acid in 1000 g. of sulfuric acid can be detected in a drop of solution by this reaction.

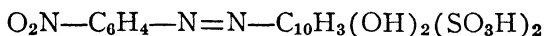
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### ***p*-NITROBENZENEAZOCHROMOTROPIC ACID**

Synonym: Chromotrope 2 $\beta$ , *p*-nitrobenzeneazo-4,5-dihydroxy-2,7-naphthalenedisulfonic acid

$C_{16}H_{11}O_{10}N_3S_2$

Mol. Wt. 469.37



**Use:** Detection of boron and germanium.

Determination of boron.

**Preparation:** Dissolve 1.38 g. of *p*-nitroaniline in a dilute solution of hydrochloric acid and cool with ice. Diazotize with a cold solution containing 0.85 g. of potassium nitrite, and then pour the resulting solution of the diazo compound slowly and with cooling into a solution of chromotropic acid in dilute sodium hydroxide. Salt out the dye which is formed with sodium chloride, and filter and dry on a porous plate. Purify the compound by dissolving in water and again salting out, or by dissolving in concentrated acetic acid and precipitating by the addition of ether.<sup>1</sup>

**Detection and determination of boron.** The blue color of a solution of *p*-nitrobenzeneazochromotropic acid in concentrated sulfuric acid is changed to a greenish-blue upon the addition of a borate or boric acid. This color change appears to be due to the formation of an inner-complex ester of boric acid, which is probably analagous to that formed in the reaction of boric acid with the hydroxyanthraquinone dyes. *p*-Nitrobenzeneazochromotropic acid is especially suitable for the formation of such complex esters, since it contains two hydroxyl groups in the peri-position. Komarovskii and Poluektov<sup>2,3</sup> have used this reaction for the detection of boron. The following procedure may be used for the detection of borate:

**Procedure.** Place a drop of a slightly alkaline solution to be tested in a porcelain dish and evaporate to dryness. While the dish is still warm, add 2-3 drops of a 0.005 per cent solution of the reagent in concentrated sulfuric acid and allow the mixture to cool. A bluish-violet or a greenish-blue color is obtained with as little as 0.08 $\gamma$  of boron in 0.04 ml. of solution.

Oxidizing agents such as nitrates and chlorates interfere with this test by giving a red or yellow color with the reagent. This interference can be eliminated, however, by reducing with a little solid hydrazine sulfate. Fluorides also interfere by preventing the formation of the colored ester, due to the conversion

of boron to fluoboric acid or boron fluoride. Fluorides are destroyed by evaporating with silicic acid and sulfuric acid, but the sensitivity of the test in the presence of fluoride or nitrate is somewhat reduced:

**Procedure.** Mix 1-2 drops of the solution to be tested in a porcelain dish with a little solid hydrazine sulfate, or with a very small quantity of silicic acid and 1-2 drops of sulfuric acid (depending upon whether oxidizing agents or fluorides are present). Heat carefully until fumes of sulfuric acid appear. While the residue is still warm, add 3-4 drops of the reagent as in the above test, and observe the color after the mixture is cool.

As little as 0.25 $\gamma$  of boron can be detected in the presence of 13,000 times as much potassium nitrate or 11,600 times as much potassium chlorate. 0.5 $\gamma$  of boron can be detected in the presence of 2,700 times as much sodium fluoride.

Stettbacher<sup>4</sup> has used a similar reaction for the colorimetric determination of boron in fertilizer or plant ash.

**Detection of germanium.** Germanic acid also gives a color reaction with a solution of *p*-nitrobenzeneazochromotropic acid in concentrated sulfuric acid, but the color change is not particularly sharp, and the reaction is less sensitive than that with quinalizarin.<sup>3</sup>

1. F. Feigl, *Qualitative Analysis by Spot Tests*, 2nd English Edition, p. 63, 224. Norde-mann, New York (1939).
2. A. S. Komarovskii and N. S. Poluektov, *Mikrochemie*. **14**, 317-20 (1934); *C.A.* **28**, 6391 (1934).
3. N. S. Poluektov, *Mikrochemie*. **18**, 48-9 (1935).
4. A. Stettbacher, *Mitt. Lebensm. Hyg.* **34**, 90-7 (1943); *C.A.* **38**, 3214 (1944).

## PHENOLPHTHALEIN

$C_{20}H_{14}O_4$

Mol. Wt. 318.31

Beil. Ref. XVIII, 143.

**Use:** Detection of cadmium, magnesium, gold, and sulfate.

Phenolphthalein is a white or faintly yellow-white crystalline powder. It is odorless and unstable in air. It melts above 258° C. It is insoluble in water, but 1 g. of the solid dissolves in 13 ml. of alcohol and about 70 ml. of ether. It is soluble in aqueous solutions of sodium or potassium hydroxide or carbonate.

**Preparation:** Mix 10 g. of phthalic anhydride, 20 g. of phenol and 8 g. of concentrated sulfuric acid and heat together at 115-120° C. in an oil bath for 8 or 9 hours. Pour while hot into 500 ml. of water, and boil until the odor of phenol is no longer apparent. Maintain the volume of the solution at about 500 ml. by the gradual addition of water. On cooling, a granular yellow precipitate forms which is removed by filtration and washed with water. Dissolve in dilute sodium hydroxide solution, filter, and acidify the filtrate with acetic acid and a few drops of hydrochloric acid. Allow to stand for some hours and

filter off the light yellow, sandy powder. Dry and purify by recrystallizing from absolute alcohol to which a little decolorizing charcoal is added. Add 1 part of the phenolphthalein to 6 parts of alcohol and 0.5 parts of charcoal and boil on a water-bath for 1 hour. Filter hot, wash with 2 parts of boiling alcohol, and evaporate to two-thirds of its original volume in a water bath. Add 8 times the quantity of cold water to the cooled solution and stir well. Allow to stand for a few seconds and filter through cloth to remove the resinous oil which separates. Heat the filtrate on a water bath to remove the excess alcohol, and recover the phenolphthalein which crystallizes in the form of a white powder.<sup>1,2</sup>

**Reactions with metals.** Sachs<sup>3</sup> and Sachs and Ryffel-Neuman<sup>4</sup> have studied the reactions of phenolphthalein with insoluble metallic hydroxides and with metallic salts, and they have reported the formation of many compounds which may have some analytical value. Holler,<sup>5</sup> for example, has found that a spot test with a 1 per cent solution of phenolphthalein in ethyl alcohol gives a crimson color with cadmium hydroxide and no reaction with cupric hydroxide. This makes possible the detection of cadmium in the presence of copper. A number of insoluble hydroxides are colored by a 1 per cent alcoholic solution of reagent due to the activated adsorption of the reagent on the hydroxide.

The following procedure may be applied to the detection of cadmium in the regular scheme of qualitative analysis:

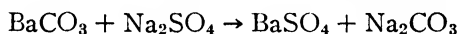
**Procedure.** Neutralize the filtrate from the lead separation with ammonium hydroxide to precipitate bismuth hydroxide, which is filtered in the usual manner. Neutralize the filtrate, which is blue if copper is present, with nitric acid and add 5 ml. of concentrated nitric acid. Evaporate to dryness and ignite the residue below a dull red heat until ammonium salts are completely volatilized. Dissolve the residue in 1.5 ml. of dilute nitric acid and dilute with water to 25 ml. Add 12 ml. of 0.5 N sodium hydroxide, filter off the precipitated hydroxide, and wash once with water. Treat the precipitate with a 1 per cent alcoholic solution of phenolphthalein and moisten with a few drops of water. A crimson color appears if cadmium is present.

Tananaev<sup>6</sup> has used phenolphthalein for the detection of magnesium. The test is carried out by moistening a strip of filter paper with an alcoholic solution of phenolphthalein and applying a drop of a neutral magnesium solution which is free from ammonium salts. The spot becomes colorless when dried over a flame, but the color returns when the spot is moistened with water. If ammonium salts are present, make the solution acid with sulfuric acid, evaporate to dryness and carefully ignite before applying the test. If alkali salts are present, add ammonium hydroxide before ignition to avoid the formation of pyrosulfate. The alkaline earth metals do not interfere.

**Detection of gold.** A 0.5 per cent alcoholic solution of phenolphthalein gives a violet color when added to a gold solution which is warmed to 35-40° C.<sup>10</sup>

**Determination of acids.** Kul'berg<sup>7</sup> has used a standard solution of sodium phenolphthaleinate for the microdetermination of acids. Small quantities of acids are titrated with this reagent. The salt is prepared by evaporating a solution of phenolphthalein in 20 per cent sodium carbonate to dryness and extracting the residue with ethyl alcohol. The pure sodium phenolphthaleinate is obtained by evaporating the alcoholic solution to dryness, again extracting with alcohol, and evaporating to dryness.

**Detection of sulfate.** Barium carbonate reacts rapidly upon warming with neutral alkali sulfates according to the following equation:



This reaction can be detected by the addition of phenolphthalein, which turns red due to the formation of the sodium carbonate. This reaction has been used by Feigl<sup>8,9</sup> as the basis for a spot test for sulfate.

**Procedure.** Mix a drop of a suspension of pure barium carbonate in a microcrucible with a drop of the neutral solution to be tested and evaporate to dryness on a water-bath. Add to the residue a drop of a 1 per cent solution of phenolphthalein in a 1:1 water-alcohol mixture. A red color appears if sulfate is present. By means of this reaction as little as 5γ of sodium sulfate can be detected at a concentration limit of 1:10,000.

Silicofluorides interfere by giving a similar reaction, but all other common anions are without effect upon this test. It is essential in making this test that the test solution be strictly neutral. When the solution is alkaline, as when testing a substance after fusion with alkali, the test is carried out by acidifying with a few drops of the test solution with hydrochloric acid, evaporating to dryness over a water-bath and then testing with barium carbonate as described above. By this procedure, the limit of identification is about 10γ.

**Detection of copper and cyanides.** Phenolphthalein is used for the preparation of phenolphthalin, which is employed as a reagent for hydrogen cyanide and copper. For details of these tests, see section on phenolphthalin.

**Preparation of phenolphthalin.** Phenolphthalein is also used in a number of analytical reactions after first reducing to phenolphthalin. These reactions are discussed in the following section.

1. A. Baeyer, *Ber.* **9**, 1230 (1876).
2. A. Baeyer, *Ann.* **202**, 68 (1880).
3. G. Sachs, *J. Am. Chem. Soc.* **62**, 3514-15 (1940); *C.A.* **35**, 999 (1941).
4. G. Sachs and L. Ryffel-Neumann, *J. Am. Chem. Soc.* **62**, 993-4 (1940); *C.A.* **34**, 3720 (1940).
5. A. C. Holler, *J. Am. Chem. Soc.* **63**, 873 (1941); *C.A.* **35**, 2810 (1941).
6. N. A. Tananaev, *Z. anal. Chem.* **88**, 93-4 (1932); *C.A.* **26**, 3454 (1932).
7. L. M. Kul'berg, *Zavodskaya Lab.* **7**, 417-21 (1938); *C.A.* **33**, 88 (1939).
8. F. Feigl, *Rec. trav. chim.* **58**, 471-80 (1939); *C.A.* **33**, 5771 (1939).
9. F. Feigl, *Qualitative Analysis by Spot Tests*, 2nd English Edition, p. 204, Nordemann, New York (1939).
10. D. C. Dalmas and E. C. Stath, *Praktika Akad. Athenon.* **10**, 106 (1935).

**PHENOLPHTHALIN**

Synonym: Phthalin, dihydroxytriphenylmethane-2-carboxylic acid

$C_{20}H_{16}O_4$

Mol. Wt. 320.33

Beil. Ref. X, 455.



**Use:** Detection of bromine, chlorine, copper ferricyanide, hydrogen cyanide, hydrogen peroxide, osmium, oxidizing agents.

Determination of copper and cyanide.

Phenolphthalin is a white crystalline powder. It melts at  $225^\circ\text{C}$ . It is insoluble in water, but is soluble in alcohol, ether and aqueous solutions of alkali hydroxides. Alkaline solutions of this compound gradually become pink upon exposure to air.

**Preparation:** The reagent is prepared by the reduction of phenolphthalein. Methods of preparation are usually given in connection with the preparation of reagent solutions for specific tests. The pure reagent may, however, be prepared as follows:

Boil phenolphthalein with zinc dust and sodium hydroxide until the solution is decolorized and then boil for an additional half hour. Dilute with water, filter, and immediately add an excess of dilute hydrochloric acid. Warm the mixture gently until the flocculent precipitate begins to crystallize and again filter. Wash with water and then treat the precipitate with alcohol. To the filtered alcoholic solution, add water until a permanent turbidity appears and allow to stand. Phenolphthalin separates from the solution on quick cooling.<sup>1,2</sup>

**Detection and determination of copper.** Thomas and Carpentier<sup>6</sup> have used the reaction of Kastle<sup>7</sup> and Meyer<sup>8</sup> for the detection of copper and for the colorimetric determination of small quantities of copper in water. A solution of 2 g. of phenolphthalin and 20 g. of pure potassium hydroxide in 100 ml. of pure water gives a pink color with a solution containing 1 part of copper in 100,000,000 parts of water. The reaction is so sensitive that distilled water which is passed through copper pipes cannot be used in the preparation of the reagent. This procedure has been studied by Muller and Burtzell.<sup>22</sup> Labat<sup>9</sup> has noted that phenolphthalin with glycerol gives a red color in the presence of copper salts.

Tixier<sup>3</sup> reports that phenolphthalin is oxidized to phenolphthalein in aqueous solutions containing traces of copper, but that the reaction is entirely prevented by the addition of 0.001 mole of hydrogen cyanide. This reaction has been confirmed by Pazienti.<sup>4,5</sup> A possible mechanism for the reaction appears to be an example of catalysis involving the formation of intermediate compounds. The sensitivity of this reaction toward copper salts depends upon conditions. A 0.01-0.001 per cent solution of copper sulfate causes an almost instantaneous oxidation of the reagent without the use of hydrogen peroxide, while solutions containing 0.0001-0.00001 per cent of copper salts are oxidized only very slowly unless hydrogen peroxide is added. The maximum dilution at which copper can be detected with phenolphthalin in the presence of hydrogen peroxide is

0.000001 per cent, and this is much more sensitive than other tests which have been proposed for copper. Manganese, cobalt, lead, iron, platinum and a number of other substances affect this reaction.

Kolthoff and Lingane<sup>10</sup> have studied the reaction of copper and phenolphthalin and report that it is highly sensitive, but that it is not very specific. They claim that it is suitable for the detection of copper in potable waters, although it cannot be used for the colorimetric determination of copper.

**Detection of hydrogen cyanide.** The red alkaline solution of phenolphthalein becomes colorless upon reduction with zinc dust, but the pink color is restored when the mixture is treated with hydrogen cyanide and a little copper sulfate.<sup>14,21,23</sup> This reaction has been used for the detection of small quantities of hydrogen cyanide. The following procedure has been recommended by Thiery:<sup>11</sup>

**Reagent. Phenolphthalin solution:** Dissolve 0.5 g. of phenolphthalein in 30 ml. of absolute alcohol, dilute with water, and add 20 g. of sodium hydroxide. Place the mixture in a porcelain vessel, and add powdered aluminum in small portions until the red color is discharged. Then add distilled water, which has previously been boiled and cooled in the absence of air, until the total volume of the liquid is 150 ml. Filter and use the filtrate as the reagent.

**Procedure.** Immerse filter paper in a 1:2,000 solution of copper sulfate, dry, and cut into strips. Moisten a strip of the copper sulfate paper with a few drops of the solution suspected of containing hydrogen cyanide, and add a few drops of the phenolphthalin reagent. In the presence of hydrogen cyanide, a pink color appears. This reaction is very sensitive.

Kolthoff<sup>12</sup> reports that as little as 0.1-0.05 mg. of cyanide per liter can be detected by this method.

Katz and Longfellow<sup>13</sup> have used a similar procedure for detection of hydrogen cyanide in air.

Various oxidizing agents have the same effect as cyanides in the above test. Chlorine, nitric acid, nitrous acid and ferric chloride react with the cupric sulfate and hydrogen peroxide. Potassium persulfate, sodium hypochlorite, sodium perchlorate and bromine also give a color reaction in an alkaline solution. Even non-oxidizing acids such as hydrochloric acid, sulfuric acid, fluosilicic acid, and phosphoric acid color the reagent solution pink after sodium hydroxide is added. All of these substances must be absent before applying the cyanide test.

**Determination of cyanide.** The pink color formed in the reaction between phenolphthalin and hydrogen cyanide in the presence of copper sulfate has been used for the colorimetric determination of cyanide. By using a modified reagent, 0.5γ of cyanide in 2 ml. of solution can be determined with an error of only about 3 per cent.<sup>25</sup>

**Reagent.** Mix 0.5 ml. of a 1 per cent solution of phenolphthalin in 99.5 ml. of a 0.01 per cent cupric sulfate solution and mix. This solution is stable for one day at room temperature.

**Procedure.** Place 1 ml. of a 0.05 per cent potassium hydroxide in a colorimeter cell, add 2 ml. of the solution to be tested, and then add 1 ml. of the reagent. Mix and determine the color. The color is stable 10 minutes.

A similar method has been used to determine as little as 0.02 p.p.m. of hydrogen cyanide in air.<sup>26</sup>

**Reactions with oxidizing agents.** Kul'berg<sup>15</sup> has used phenolphthalin for the detection of oxidizing agents. The presence of an oxidizing agent is indicated by a color reaction with phenolphthalin which appears when a strong base is added to the solution buffered to pH 5.5. Phenolphthalin is recommended as one of the better reagents for the detection of traces of osmium tetroxide, since it yields a colored oxidation product.<sup>16</sup>

Kniga<sup>17</sup> has used phenolphthalin for the detection of ferricyanide. A drop of the solution to be tested is treated on a strip of filter paper with a drop of an alkaline solution of phenolphthalin. A brilliant red color is formed if ferricyanide is present.<sup>24</sup> Permanganate and persulfate interfere with this test. An excess of ammonium salt decolorizes the spot and lowers the sensitivity of the reaction.

Stamm<sup>18,19</sup> has used the Meyer<sup>8</sup> phenolphthalin reagent for the detection of hydrogen peroxide or organic peroxides in ethers.

**Reagent.** Dissolve 1-2 g. of phenolphthalein and 25 g. of potassium hydroxide in 100 ml. of water, and add 1 g. of zinc dust and gently heat until the solution is decolorized. Filter.

**Procedure.** Mix 1 drop of the reagent with 2 drops of 1:2,000 copper sulfate solution and then add 1 ml. of the ether to be tested. If the ether is undecomposed (absence of peroxides), the reagent remains colorless, but in the presence of peroxides a pink to intense red ring is formed at the junction of the two liquids.

Schales<sup>20</sup> has studied the phenolphthalin reaction for peroxides and reports that its use is not limited to the analysis of colorless mixtures. Where the color of the phenolphthalein, which is formed in the presence of hydrogen peroxide, is obscured by the color of the solution, the phenolphthalein can be detected by a characteristic absorption in the green part of the spectrum (563.3-544  $m\mu$ ). Hydrogen peroxide converts the phenolphthalin to phenolphthalein even at pH values where the phenolphthalein is still colorless. The addition of alkali after the completion of the reaction shows the presence of phenolphthalein. By means of a test tube reaction, peroxide can be detected at a dilution of 1:100,000,000. A spot test is less sensitive, but with 0.04 ml. (1 drop), hydrogen peroxide can be detected at a concentration of 1:1,000,000.

1. F. F. Blicke and O. J. Weinkauff, *J. Am. Chem. Soc.* **54**, 1458 (1932).
2. A. Baeyer, *Ann.* **202**, 80-3 (1880).
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4. U. Pazienti, *Boll. chim. pharm.* **51**, 661-6 (1912); *C.A.* **7**, 2170 (1913).
5. U. Pazienti, *J. Chem. Soc.* **104**, II, 154 (1913); *C.A.* **7**, 2170 (1913).
6. P. Thomas and G. Carpentier, *Compt. rend.* **173**, 1082-85 (1921); *C.A.* **16**, 538 (1922).



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8. Meyer, *Munchen. med. Wochenschr.* **50**, 1492 (1903).
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10. I. M. Kolthoff and J. J. Lingane, *Mikrochemie Festschr. von Hans Molisch.* 274-8 (1936); *C.A.* **31**, 4226 (1937).
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12. I. M. Kolthoff, *Pharm. Weekblad.* **54**, 1157-71 (1917); *C.A.* **12**, 30 (1918).
13. S. H. Katz and E. S. Longfellow, *J. Ind. Hyg.* **5**, 97-104 (1923); *C.A.* **17**, 2686 (1923).
14. J. Stamm, *Pharmacia (Bull. assoc. des pharmaciens d'Esthonie)* **18** (1924); *J. pharm. chim.* **30**, 203-4 (1924); *C.A.* **19**, 1549 (1925).
15. L. M. Kul'berg, *J. Applied Chem. (U.S.S.R.)*. **10**, 1130-34 (1937); *C.A.* **32**, 2868 (1938).
16. L. M. Kul'berg, *J. Gen. Chem. (U.S.S.R.)*. **8**, 1139-42 (1938); *C.A.* **33**, 4899 (1939).
17. A. G. Kniga, *J. Applied Chem. (U.S.S.R.)*. **10**, 946 (1937).
18. J. Stamm, *Pharmacia*. 8 pp. (Sept. 1924).
19. E. Tikkanen, *Farm. Revy.* 627 (1926).
20. O. Schales, *Ber.* **71B**, 447-60 (1938); *C.A.* **32**, 3294 (1938).
21. F. Weehuizen, *Pharm. Ztg.* 282 (1905).
22. R. H. Muller and A. T. Burtzell, *Mikrochem. ver. Mikrochim. Acta.* **28**, 209-28 (1940); *C.A.* **34**, 7776 (1940).
23. L. Chelle, *J. pharm. chim.* **19**, 361 (1919); *Bull. soc. pharm. Bordeaux.* 70 (1919); *C.A.* **13**, 2494 (1919).
24. L. N. Lapin, *Trudy Uzbekskogo Gosudarst. Univ. Sbornik Rabot Khim.* **15**, 150-68 (1939); *C.A.* **35**, 4305 (1941).
25. W. A. Robbie, *Arch. Biochem.* **5**, 49-58 (1944); *C.A.* **39**, 2467 (1945).
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## PHENOL RED

Synonym: Phenolsulfonphthalein, sulfenthal

$C_6H_{14}O_5S$

Mol. Wt. 354.36

Beil. Ref. XIX, 91 (649).

**Use:** Detection and determination of bromine.

Phenol red is a bright red to dark red crystalline powder. It is stable in air. One g. of the solid dissolves in about 1.5 liters of water, 350 ml. of alcohol, or 500 ml. of acetone. It is almost insoluble in chloroform and ether. It dissolves readily in solutions of the alkali hydroxides or carbonates with the formation of a red color. This is discharged by boiling with zinc dust.

**Detection and determination of bromine.** Phenol red, with a color change of yellow to red pH 6.4-8.0, reacts with a dilute solution of a hypobromite to form an indicator of the bromophenol blue type, which changes from yellow to blue-violet at pH 3.2-4.6. The oxidation of bromides, and the subsequent bromination of phenol red, takes place readily in the presence of calcium hypochlorite in a borax buffer at a pH of 8.7-8.8. By making a color comparison at pH 5.0-5.4 all unbrominated phenol red is in the yellow form, and the brominated compound is reddish-brown to violet in color; in this way the reagent serves for the colorimetric determination of bromide. This procedure may be used to determine 1-4% of bromide in 1.0 ml. of solution.<sup>1</sup> The following method has been proposed by Balatre:<sup>2</sup>

**Reagents. Solution A. Phenol red:** Dissolve 33 mg. of phenol red in 3 ml. of 0.1 N sodium hydroxide, and dilute with water to 100 ml.

**Solution B. Buffer solution** (pH = 5.0): Mix 500 ml. of N sodium hydroxide and 650 ml. of N acetic acid.

**Solution C:** Mix 25 ml. of Solution A with sufficient Solution B to make 500 ml. of solution.

**Solution D:** 0.005 N chloramine solution.

**Solution E:** 0.1 N sodium thiosulfate.

**Procedure.** Place 5 ml. of a solution containing 5-10 $\gamma$  of bromide ion in 30 ml. of solution in a beaker, and add 2 ml. of Solution A. Measure 2 ml. of Solution D into a small test tube, and pour this quickly into the beaker and stir. Allow to stand 15 seconds, and then stop the reaction by addition of 3-5 drops of Solution E. Wash the mixture into a 10-ml. graduated cylinder and fill to the mark (10 ml.), and measure the color in a Pulfrich Photometer, or by comparison with color standards.

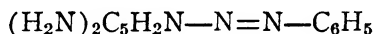
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## PHENYLAZODIAMINOPYRIDINE

$C_{11}H_{11}N_5$

Mol. Wt. 213.20

Beil. Ref. XXII, (701).



**Use:** Detection and differentiation of chromate and dichromate.

This compound consists of yellow-orange needles which melt at 137° C. It is soluble in water with an orange-yellow color and in acids with a somewhat redder color.

**Preparation:** Phenylazodiaminopyridine hydrochloride is prepared from benzenediazonium chloride and 2,6-diaminopyridine hydrochloride in the presence sodium acetate.<sup>1</sup>

**Detection and differentiation of chromate and dichromate.** An intensely yellow-colored precipitate is obtained when a 1 per cent solution of phenylazodiaminopyridine hydrochloride is added to a solution containing chromate ions, and an orange-yellow precipitate is obtained with solutions containing dichromate ions. The sensitivity of this reaction is 2 $\gamma$ , and the limiting concentration is 1:5000 for both tests. It is possible to identify the two ions in a mixture if the quantity of either does not exceed 50 times that of the other.<sup>2</sup>

1. A. E. Tschitschibabin and O. A. Seide, *J. Russ. Phys.-Chem. Ges.* **50**, 522-3 (1918).
2. A. Martini, *Pub. inst. investigaciones microquim. Univ. nacl. litoral (Rosario, Argentina)* **4**, 25-9 (1940); *C.A.* **36**, 366 (1942).

**PHENYLIMINO-8-DINAPHTHOXAZINE** $C_{26}H_{16}N_2O$ 

Mol. Wt. 372.39

**Use:** Detection of nitric acid.

This compound is a red crystalline solid, melting at 321° C. It forms a violet solution in alcohol, hydrochloric acid and concentrated sulfuric acid. It is only slightly soluble in alcohol, benzene and toluene.

**Preparation:** Heat a mixture of 5 g. of di-(phenylimino)-1,4-hydroxy-2-naphthoquinone-1,4, and 4.5 g. of  $\beta$ -naphthylamine and 25 ml. of xylene on a boiling water bath and pass air into the mixture. After 45 minutes, filter, and wash the precipitate with boiling methyl alcohol. Dry and recrystallize from pyridine.<sup>1,2</sup>

**Detection of nitric acid.** Lantz<sup>1-3</sup> has shown that dissymmetrical arylimino-8-dinaphthoxazines dissolved in concentrated sulfuric acid turn violet when treated with small quantities of nitric acid. A solution containing 0.2 g. of the oxazine in 1000 g. of 93 per cent sulfuric acid is a satisfactory reagent. As little as 50 mg. of nitric acid in 1000 g. of sulfuric acid can be detected in a drop of solution by this reaction.

1. R. Lantz, *Ann. chim.* [11] 2, 58-99 (1934).
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**QUINOLINE BLUE**

Synonym: Cyanin

 $C_{20}H_{35}N_2I \cdot 1\frac{1}{2}H_2O$ 

Mol. Wt. 565.52

Color Index, 806.

**Use:** Detection of iodine.

This dye consists of glistening green needles, which are insoluble in cold, and sparingly soluble in hot water. The aqueous solution is blue-violet in color.

**Preparation:** Quinoline blue is formed when isoamyl iodide and a mixture of equal molecular proportions of quinoline and lepidine are treated with sodium hydroxide.

**Detection of iodine.** Quinoline blue is used for the microchemical detection of free iodine in plant tissues. The dye is colored brown by free iodine.

1. A. Golenkin, *Z. wiss. Mikroskop.* 553 (1894).

**RESAZURIN**

Synonym: Resazoin, "Diazoresorcinol"

 $C_{12}H_7O_4N$ 

Mol. Wt. 229.18

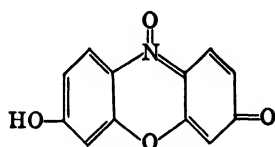
Beil. Ref. XXVII, 128.

**Use:** Detection of hyposulfite (sulfoxylate).

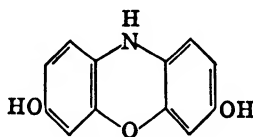
Resazurin consists of dark red, small crystals with a greenish luster. It is insoluble in water and ether, is only sparingly soluble in alcohol, glacial acetic acid, and is soluble in dilute alcoholic hydroxides.

**Preparation:** Resazurin is prepared by allowing fuming nitric acid to act several days on an ether solution of resorcinol.<sup>1</sup>

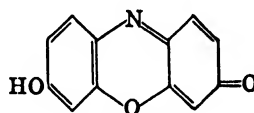
**Detection of hyposulfite.** Resazurin, whose blue alkaline solution may show a slight brownish red fluorescence, can be reduced in an acid or alkaline solution to hydroresorufin (which is easily oxidized to resorufin) or resorufin. The red alkaline solution of the latter shows an intense yellow-red fluorescence. Consequently substances capable of reducing action can be detected by the conversion of resazurin to resorufin. The formulas for these compounds are as follows:



Resazurin



Hydroresorufin



Resorufin

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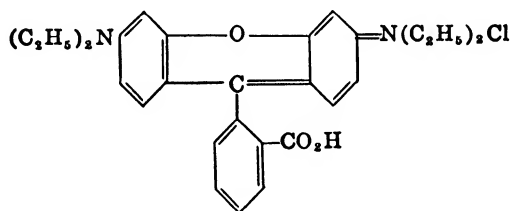
## RHODAMINE B

Synonym: Tetraethylrhodamine

$C_{28}H_{31}O_3N_2Cl$

Beil. Ref., 346 (785). Color Index, 749.

Mol. Wt. 479.00



**Use:** Detection of antimony, bismuth, cobalt, columbium, gold, manganese, mercury, molybdenum, tantalum, thallium and tungsten.

Determination of antimony and tungsten.

Rhodamine B consists of green crystals or a reddish-violet powder. It is very soluble in water with the formation of a bluish-red solution. Very dilute solutions are strongly fluorescent. The dye is also soluble in alcohol, and slightly soluble in hydrochloric acid and sodium hydroxide solutions.

**Preparation:** Heat 10 g. of diethyl-*m*-aminophenol with 12 g. of phthalic anhydride at 170-75° C. until the melted product becomes crystalline. Cool, grind to a fine powder, and digest for several hours with 10 g. of 18 per cent ammonia and 160 ml. of water at ordinary temperature. Extract with benzene and remove the dye from the united benzene solution by extraction with hot

dilute hydrochloric acid. The hydrochloride separates on cooling of the aqueous solution as small green crystals.

**Detection of antimony.** When pentavalent antimony salts are added to aqueous solutions of the xanthone dyes, which are usually red in color, the color is changed to violet or blue with the formation of a finely divided precipitate. The composition of these compounds has not yet been determined, although they appear to be the result of oxidation reactions. Of the various xanthone dyes studied, rhodamine B appears to be the most suitable for detecting antimony, particularly in testing for small quantities of antimony in the presence of large quantities of tin.<sup>1</sup>

The following procedure is used for detecting antimony in the absence of interfering substances:

**Reagent.** Dissolve 10 mg. of rhodamine B in 100 ml. of water.

**Procedure.** Place 1 ml. of the reagent in the depression of a spot plate, and add 1 drop of the solution to be tested which has been made strongly acid with hydrochloric acid and oxidized by means of sodium nitrite. If antimony is present, the light red fluorescent dye solution is changed to violet. This test serves to detect 0.5γ of antimony at a dilution of 1:100,000, and in the presence of 12,500 times as much tin.

The rhodamine B test has been rather widely used as a confirmatory test for antimony in systematic schemes of analysis.<sup>2-6,10-21,24</sup>

In the usual procedures of systematic analysis trivalent antimony is formed along with stannic tin when the sulfides are dissolved in hydrochloric acid. Consequently it is necessary to oxidize the antimony to the pentavalent state by means of sodium nitrite.

Small quantities of iron do not interfere with the test but mercury, gold and thallium chlorides, and any bismuth chloride which is precipitated by hydrolysis, give a similar coloration. Molybdate and tungstate in acid solutions also give colors similar to that with antimony. Lead, vanadium, columbium, tantalum, and uranium do not give colorations with rhodamine B, but if a concentrated solution of the reagent is used, precipitates are obtained with iodide, bromide, thiocyanate, dichromate, persulfate, permanganate, perchlorate, and thiosulfate.

Miller and Lowe<sup>6</sup> have used rhodamine B as a confirmatory test for antimony in a scheme of analysis, but claim to have increased the sensitivity of Eegriwe's test<sup>1</sup> by carrying out the reaction in a solution which is 3 N in hydrochloric acid, and by using a 1 per cent solution of rhodamine B in 3 N hydrochloric acid. Upon adding a drop of a saturated aqueous solution of potassium nitrite and a drop of the reagent to 0.5 ml. of a solution containing 50γ of antimony, a reddish-purple color appears, which becomes blue in transmitted light. Eventually a finely divided red precipitate forms. The test is still positive with as little as 5γ of antimony in 0.5 ml. of solution. If the supernatant liquid is not pink after adding the reagent, an insufficient quantity has

been added. A large excess of tin, bismuth, lead, tellurite, molybdate, tartaric acid and phosphoric acid do not interfere. Molybdate gives a deep red color but no precipitate.

Rosenthaler <sup>7</sup> has used a modification of Eegriwe's test <sup>1</sup> for the detection of antimony. If stibine,  $\text{SbH}_3$ , which is formed by reduction of antimony compounds with zinc and hydrochloric acid is brought into contact with a drop of a rhodamine-mercuric chloride solution, a red crystalline precipitate forms. This test is sensitive to 1 $\gamma$  of antimony at a dilution of 1:100,000. The reagent is a mixture of 1 part of 0.1 per cent rhodamine B solution and 9 parts of 1 per cent mercuric chloride solution.

**Determination of antimony.** Pentavalent antimony in a solution strongly acid with hydrochloric acid, or with sulfuric acid and containing chloride ion, reacts with rhodamine B to form a dark red compound which is insoluble in water. The suspension has a bluish-purple fluorescence, and when precipitated in the presence of a protective colloid such as gum gatti, appears blue in a colorimeter. Under proper conditions the reaction appears to be quantitative. The compound formed is soluble in many organic solvents, is easily filtered, and is unusually stable. The composition of this compound is not known, but one atom of antimony appears to be associated with one molecule of rhodamine B, possibly as a complex salt. The presence of the chloride ion has been found to be absolutely essential to the reaction, and chloride is present in the precipitated compound.

The colored compound can be formed in a 50 per cent hydrochloric acid solution, but a 25 per cent sulfuric acid solution containing chloride is preferred for the colorimetric determination. In the qualitative test described above, in which the antimony was oxidized with sodium nitrite prior to treatment with rhodamine B, a violet color appears, but a quantitative procedure has not been developed from this method because of interference due to the excess sodium nitrite and reagent in the solution at the completion of the reaction.

The choice of oxidizing agents for converting trivalent to pentavalent antimony is somewhat limited. An excess of sodium nitrite, which interferes with the reaction, can be destroyed with urea, but under some circumstances the nitrate formed by the reaction interferes with the test. Sodium chlorite is satisfactory and is preferred if the reaction is carried out in hydrochloric acid. The excess reagent is easily destroyed with hydroxylamine hydrochloride. When the reaction is carried out in sulfuric acid solution, ceric sulfate is recommended. This oxidizing agent serves as its own indicator, and the excess is easily removed by treatment with hydroxylamine hydrochloride. A slight excess of ceric or cerous ion, however, influences the final color.

The excess reagent, which also interferes with the determination, is destroyed by treating with bromine.

The following procedure has been described by Frederick: <sup>8</sup>

**Reagents.** *25 per cent sulfuric acid:* Dilute 125 ml. of sulfuric acid to 500 ml. with distilled water.

*0.1 N ceric sulfate solution:* Dissolve 3.3 g. of anhydrous ceric sulfate in sufficient 3 per cent sulfuric acid to make 100 ml. of solution.

*0.1 N sodium thiosulfate solution:* Dissolve 2.5 g. of sodium thiosulfate pentahydrate in sufficient water to make 100 ml. of solution.

*Lithium chloride solution:* Dissolve 25.5 g. of lithium chloride in sufficient water to make 100 ml. of solution.

*Rhodamine B solution:* Dissolve 1 g. of rhodamine B in 500 ml. of distilled water and filter.

**Procedure.** The antimony must be in an approximately 25 per cent sulfuric acid solution. Transfer 1-5 ml. of the sample, which should contain 50-250 $\gamma$  of antimony to a 50-ml. glass stoppered graduated cylinder and dilute to 5 ml. with 25 per cent sulfuric acid solution. Add the acid from a buret by allowing to flow down the sides of the cylinder. Add 1 ml. of lithium chloride solution, mix well, and then add 0.1 N ceric sulfate solution until a pale yellow color persists. This requires approximately 2 drops of the oxidizing agent. Mix with sufficient 1 per cent hydroxylamine hydrochloride solution to discharge the yellow color. This requires approximately 2 drops of the reducing agent. Cool the mixture in an ice-bath for 15 minutes, and after removing from the bath add 1 ml. of 0.2 per cent rhodamine B solution from a 25-ml. buret. Again mix and cool in an ice-bath for 10 minutes. Add 10 ml. of water, and once more cool in an ice-bath for 10 minutes. Remove from the bath, and add 2 drops of saturated bromine water. Mix quickly, and immediately add 2 drops of 0.1 N sodium thiosulfate solution and mix. Immediately add 20 ml. of alcohol, shake well, dilute to 50 ml. with distilled water, and again shake. Allow the mixture to stand for 30 minutes and compare the resulting color with that obtained by treating solutions of known antimony content in a similar manner. The color comparison is best carried out in a colorimeter.

When the total quantity of antimony in the sample does not exceed 25 $\gamma$  use only 0.5 ml. of Rhodamine B solution and carry out the comparison in a Nessler tube using the standard series procedure.

The amount of reagent solution required depends upon the antimony content of the sample. The amount of the solution to be used is determined by reference to Table 65:

TABLE 65.

Antimony Content of Sample $\gamma$	Rhodamine B Reagent Required ml.
0-50	0.5
50-150	1.0
150-200	1.5
200-300	2.0

Practically all acid radicals except chloride and sulfate interfere somewhat with this determination. Metals such as mercury, copper, nickel, cadmium and zinc interfere, but these can be removed by a preliminary extraction of the sample at pH 8.5, using a solution of 100 mg. of dithizone per liter of carbon tetrachloride. The effect of several metallic ions, salts and acids upon the antimony determination with rhodamine B is shown in Table 66.

**Detection and determination of tungsten.** In dilute hydrochloric acid solution, tungstates cause the yellowish-red color of a dilute solution of rhodamine B to change to violet.<sup>1</sup> This reaction has been used by Heyne<sup>9</sup> for the colorimetric determination of small quantities of tungsten. Molybdenum also reacts with Rhodamine B to give a similar color, but approximately 10-20 times as much molybdenum as tungsten is required to give the test. For this reason the rhodamine B method is better than hydroquinone for the determination of tungsten, since the latter reagent also gives a color reaction with molybdenum at about the same concentration.

**Procedure.** Evaporate an acid solution of the sample to a small volume to remove volatile acids, and then neutralize and finally evaporate to 0.5 ml. Add 1 drop of concentrated hydrochloric acid and 2 ml. of a solution prepared by dissolving 0.1 g. of rhodamine B in a liter of water. Compare by means of a series of standards with solutions of known tungsten content which have been similarly and simultaneously prepared. Compare by both reflected and transmitted light. An accuracy of only 20-33 per cent can be claimed for this method.

The color obtained in the above reaction is stable for about one hour when the mixture is exposed to air. After a time violet flocks separate from the solution.

Hydrochloric acid interferes with this determination if present in great excess although sodium chloride and silicates are without effect.

Oats<sup>10</sup> has suggested the substitution of rhodamine B for cinchonine in the usual tungsten analysis. The following procedure illustrates this use.

**Reagents.** *Rhodamine B solution:* Dissolve 1 g. of rhodamine B in 100 ml. of distilled water. Break up the lumps to complete solution, heat to boiling, and filter through close texture paper without washing. About 1 ml. of this solution should be added for each 10 mg. of  $WO_3$ , and an excess of 1.5 ml. should be added.

*Rhodamine B wash solution:* Add 2.5 ml. of the rhodamine B precipitating solution and 6 ml. of hydrochloric acid to 2 liters of water.

*Ammonia solution:* To 1780 ml. of water, add 20 ml. of concentrated hydrochloric acid, and then add 200 ml. of concentrated ammonium hydroxide solution.

**Procedure.** Grind the material to be analyzed until it passes a 150-mesh sieve, and moisten the resulting powder in a 250-ml. beaker with water. Add 50 ml. of concentrated hydrochloric acid, and allow to stand on a hot plate for three hours with occasional stirring, and finally evaporate to 25 ml. Remove



TABLE 66.—100 $\gamma$  OF Sb<sup>v</sup> IN SAMPLE

Substance	Amount mg.	Interference Effect	Substance	Amount mg.	Interference Effect
H <sub>3</sub> PO <sub>4</sub>	200.0	None	Ce	1.0 <sup>a</sup>	Off color
Al	7.5	None	Hg	0.5 <sup>a</sup>	Deepens color
Mn	7.5	None	Cd	3.0 <sup>a</sup>	Deepens color
Bi	7.5	None	Zn	3.5 <sup>a</sup>	Deepens color
CaSO <sub>4</sub>	Saturated solution	None	KClO <sub>4</sub>	Trace <sup>a</sup>	Deepens color
Mg	7.5	None	Sn	3.5 <sup>a</sup>	Deepens color
PbSO <sub>4</sub>	Saturated solution	None	HClO <sub>4</sub>	Trace <sup>a</sup>	Deepens color
Fe	4.0 <sup>a</sup>	Off color	Cu	Trace <sup>a</sup>	Weakens color
As <sup>III-V</sup>	Trace <sup>a</sup>	Off color	Ni	7.5 <sup>a</sup>	Weakens color
NaNO <sub>3</sub>	1.0 <sup>a</sup>	Off color	NaNO <sub>2</sub>	Trace <sup>a</sup>	Weakens color
NaF	1.0 <sup>a</sup>	Off color	NaBr	0.5 <sup>a</sup>	Weakens color
Tl	Trace <sup>a</sup>	Off color	H <sub>2</sub> O <sub>2</sub>	Trace <sup>a</sup>	Weakens color

<sup>a</sup> Maximum permissible amounts per samples containing 100 $\gamma$  of antimony.

from the hot plate and add 10 ml. of concentrated nitric acid and evaporate to 8 ml. Add 100 ml. of boiling water with stirring, and allow to stand at the boiling point for several minutes. Add a solution of the reagent with constant stirring, and boil to coagulate the precipitate. Filter, wash twice with rhodamine B wash solution, and then wash well with 2 per cent hydrochloric acid.

Return the filter paper to the original beaker and add 20 ml. of water and 7 ml. of ammonium hydroxide. Macerate the paper and rinse the beaker with warm ammonium hydroxide wash solution. Replace the cover and heat 5-10 minutes with occasional stirring. Again filter and wash with warm ammonium hydroxide wash solution. Evaporate carefully to approximately 100 ml., and again add rhodamine B solution. Stir while adding dropwise concentrated hydrochloric acid until a permanent precipitate is formed, and then add an additional 2 drops of the concentrated acid. Add filter paper pulp, stir well, and heat to boiling. Allow the precipitate to settle, filter, and wash.

Ignite the precipitate in a porcelain crucible at a low heat, cool, transfer the residue to a weighed platinum crucible, and ignite at  $750^{\circ}\text{C}$ . for 5 minutes. Cool, add 1 drop of water and 1 ml. of hydrogen fluoride, and evaporate to dryness on a hot plate. Again ignite, cool and weigh as  $\text{WO}_3$ .

Box <sup>22</sup> reports that rhodamine B is superior to cinchonine for the precipitation of tungstic oxide from an acid solution. According to Lambie,<sup>23</sup> however, the method of Box is not suitable for general application.

**Detection of gold.** Gold may be detected by the reddish-purple precipitate which forms when rhodamine B is added to a hydrochloric acid solution containing gold salts.<sup>11</sup> The reagent used is a 1 per cent solution of rhodamine B in 3 N hydrochloric acid. The test is carried out by adding a drop of the reagent to 0.5 ml. of the solution to be tested. As little as  $1\gamma$  of gold can be detected in 0.05 ml. of 3 N hydrochloric acid. The test can be carried out in the presence of 500 times as much mercury. As little as  $5\gamma$  of gold in 1 drop of 3 N hydrochloric acid can be detected in the presence of 1000 $\gamma$  of platinum, 300 $\gamma$  of palladium and 50 $\gamma$  of rhodium or iridium.

The reddish fluorescence of rhodamine B in an acid solution which is observed under ultra-violet light disappears upon the addition of a solution of gold salts. This reaction has been used by Goto <sup>12,13</sup> for the detection of gold.

**Detection of thallium.** Miller <sup>14</sup> has used rhodamine B for the detection of thallium in the analysis of an analytical group consisting of lead, silver, thallium and bismuth (system of Noyes and Bray). The procedure consists of the following steps: Precipitate the metals as  $\text{PbBr}_2$ ,  $\text{TlBr}$ ,  $\text{AgBr}$  and  $\text{BiOBr}$ , boil with 0.5 ml. of 9 N hydrobromic acid and bromine to form trivalent thallium. Dilute the mixture with 1 ml. of water and centrifuge to remove silver bromide. To 0.5 ml. of the solution, add 0.05 ml. of 9 N hydrobromic acid and a little disodium arsenite solution. Then detect thallium by adding an excess of 1 per cent rhodamine B in 3 N hydrobromic acid. A red precipitate is a positive test for thallium.

Egriwe first used rhodamine B as a sensitive reagent for thallium, and Miller and Lowe <sup>6,11</sup> have enhanced the sensitivity of the rhodamine B reagent

by using in a fairly concentrated hydrochloric acid solution. For the detection and estimation of small quantities of thallium in the presence of large amounts of lead, excellent results have been obtained by substituting 3 N hydrobromic acid, in which lead bromide is somewhat soluble. As little as  $2\gamma$  of thallium can be detected in 1 ml. of 3 N hydrobromic acid solution containing 10 mg. of lead or bismuth and sufficient silver bromide to saturate the solution. Bromine, which forms a red precipitate with rhodamine B, is destroyed by the addition of sodium arsenite, which does not reduce thallium in a strongly acid solution.

Trivalent thallium changes the fluorescence of rhodamine B from red to violet, and Goto<sup>12,13</sup> has used this reaction for the detection of as little as  $0.5\gamma$  of thallium.

**Detection of columbium and tantalum.** According to Shapiro,<sup>15</sup> as little as  $0.2\gamma$  of tantalum or columbium can be detected by the violet color and the flaky precipitate which forms with rhodamine B. Molybdenum, tungsten, mercury, gold, antimony and iron are said to interfere. Dobina and Platonov<sup>16</sup> say, however, that the color reactions proposed by Shapiro are unsatisfactory because of their low sensitivity.

**Detection of cobalt, manganese and tungsten.** Rhodamine B gives a strong reddish-brown fluorescence in an acid or basic solution. If a solution of the reagent is made basic in the presence of manganese, a faint green fluorescence appears, and the original fluorescence of rhodamine B does not return when the solution is made acid. As little as  $0.1\gamma$  of manganese can be detected by this behavior.<sup>12,17</sup>

Cobalt behaves in a manner very similar to that of manganese. As little as  $2.5\gamma$  of cobalt can be detected in this way.<sup>17</sup>

The reddish fluorescence of rhodamine B in an acid solution is discharged by the addition of as little as  $2.5\gamma$  of tungsten. This reaction has been used by Goto<sup>17</sup> to detect small quantities of tungsten.

**Detection of bismuth, mercury and molybdenum.** Bismuth, mercury and molybdenum give reactions with rhodamine B similar to that with antimony and the reagent. In this way as little as 0.01 mg. of molybdenum and 0.007 mg. of bismuth can be detected. The mercury reaction is only sensitive to 1 mg. per ml. of solution.

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### ROSINDULIN 2B BLUISH (K)

$C_{28}H_{17}N_3O_9S_3Na_2$

Color Index, 829.

**Use:** Detection of chlorine.

The dye is a red powder. It dissolves in hot water to form an orange-red solution, which gelatinizes on cooling.

**Preparation:** Rosindulin 2B bluish (K) is prepared by sulfonating phenyl-rosindulin with four parts of fuming sulfuric acid (21 per cent) until a sample dissolves completely in 40 parts of water. The resulting trisulfonate is converted to the acid sodium salt.<sup>1</sup>

**Detection of chlorides and chlorine.** Rosindulin 2B Bluish (K) may be used to detect small quantities of chloride and chlorine.<sup>2</sup>

**Procedure.** Immerse a strip of filter paper in a red aqueous solution of the dye, and hold over the mouth of a test tube containing the material suspected of containing chloride, some manganese dioxide and sulfuric acid. If chloride is present, a yellow spot appears on the paper. Dry over a gas flame, and hold for a short time at the mouth of a bottle containing concentrated hydrochloric acid. The yellow spot turns blue. As little as 0.002 mg. of chlorine gives this test.

The action of chlorine on the paper must be interrupted with the appearance of the yellow color, since otherwise a further reaction causes the formation of a yellow dye which is not changed to the blue color.

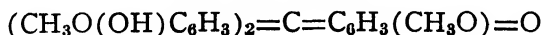
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### RUBROPHEN

Synonym: Trimethoxydihydroxyoxotriphenylmethane

$C_{22}H_{20}O_6$

Mol. Wt. 380.38



**Use:** Detection of nitrate.

Rubrophen is a red dye which is only slightly soluble in water, but readily soluble in alkali. A dilute alkaline solution is violet in color.

**Detection of nitrate.** Nitrate may be detected by its reaction with rubrophen: <sup>1,2</sup>

**Reagent.** Dissolve 3 mg. of rubrophen in 10 ml. of 0.1 N sodium hydroxide solution, and add slowly 12 ml. of 0.1 N sulfuric acid. Finally dilute with water to 100 ml. This solution, which is orange in color, contains 1γ of rubrophen in each drop.

**Procedure.** Place 0.5 ml. of concentrated sulfuric acid in each of two depressions on a porcelain plate, and to each add 0.03 ml. of the above reagent by means of a micropipet. To the pink mixture in one of the depressions add 0.03 ml. of a dilute solution suspected of containing nitrate and stir with a glass rod. If the solution contains nitrate, the pink color disappears. By this reaction 0.6γ of nitrate can be detected at a concentration of 1:50,000.

Nitrite gives the same reaction, but other ions usually do not interfere in concentrations below 1:1,000.

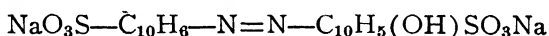
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## SERICHROME BLUE R

$C_{20}H_{12}N_2O_7S_2Na_2$

Mol. Wt. 820. 24

Color Index, 180.



**Use:** Detection and determination of chromium.

Serichrome blue R is a reddish-brown powder. It dissolves in water to form a bluish-red solution.

**Preparation:** This dye is prepared by coupling diazotized  $\alpha$ -naphthylamine-4-sulfonic acid with  $\alpha$ -naphthol-5-sulfonic acid.

**Detection and determination of chromium.** Spencer <sup>1</sup> has proposed the following method for the detection of chromium.

**Reagent.** Treat 2 g. of wool with a mixture of 40 ml. of water, 0.1 g. of sodium sulfate, and 0.02 g. of sulfuric acid. Dye the wool with 20 ml. of a solution prepared by dissolving 0.1 g. of serichrome blue R in 200 ml. of water. Stir and heat on a steam-bath for 20 minutes, and then filter with suction. Wash free of acid and allow to dry. The wool becomes a bright-crimson with a slight bluish tint.

**Procedure.** Separate iron, chromium and aluminum as the hydrous oxides and filter. Treat the precipitate with 30 ml. of water, 3 ml. of N sodium hydroxide, and 5 ml. of hydrogen peroxide to convert chromium to the soluble

chromate. Allow the mixture to stand for 30 minutes, heat to decompose the excess peroxide and filter. Acidify the filtrate with sulfuric acid and add 3 ml. of N sulfuric acid in excess. Then add with stirring 0.1 g. of the prepared wool reagent, and heat on a steam-bath for 30 minutes. If chromium is present, the color of the wool is changed to blue tint. If the color is not too dark, chromium may be approximately estimated by comparing with standard solutions similarly treated.

Molybdic, tungstic, vanadic and permanganic acids and manganous and ferrous sulfates do not interfere.

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### SOLOCHROME BLACK 6BFA

Synonym: 4-Sulfo-2-hydroxy- $\alpha$ -naphthyleneazo- $\alpha$ -naphthol, sodium salt

$C_{20}H_{13}O_5N_2SNa$

Mol. Wt. 416.36

Color Index, 201.

**Use:** Detection of aluminum and gallium.

Solochrome black 6BFA is obtained as a brownish-black powder. It dissolves in hot water to form a blackish-violet solution. It forms a cherry-red solution in alcohol, and a dark blue solution in sulfuric acid.

**Preparation:** Diazotize 24 g. of 1-amino-2-naphthol-4-sulfonic acid, and add the resulting diazo compound to a solution of 15 g. of  $\alpha$ -naphthol in 100 g. of sodium hydroxide ( $d = 1.33$ ) at  $15^\circ C$ . The mixture crystallizes after a time. Add 500 ml. of water, and neutralize with hydrochloric acid.

**Detection of aluminum and gallium.** In the absence of cobalt, chromium, iron, and fluoride, solochrome black 6BFA gives a blood-red fluorescence in acetic acid solution under ultra-violet light in the presence of either aluminum or gallium. This reaction has been used by Radley<sup>1</sup> for the detection of these metals. The test is carried out as a drop reaction as follows:

**Reagent.** Dissolve 0.1 g. of the dye in 50 ml. of water and dilute with an equal volume of ethyl alcohol.

**Procedure.** To 1 drop of the solution to be tested, add 1 drop of glacial acetic acid and 1 ml. of the reagent. Boil 15 seconds. Cool, and examine under filtered ultra-violet light. A bright, blood-red fluorescence appears with either aluminum or gallium. Use a blank with low concentrations of the metal. As little as 5 $\gamma$  of gallium or 0.5 $\gamma$  of aluminum can be detected in this way.

To eliminate interference by iron, cobalt, chromium, fluoride, and other ions, proceed as follows: Mix 1 ml. of the solution to be tested with 1 drop of 10 per cent sodium silicate solution, and evaporate to dryness on a water bath. Add 1 drop of concentrated sulfuric acid, and evaporate to dryness over a small flame. Add to the residue 1 ml. of water and 1 ml. of N sodium hydroxide, and then boil and filter. Neutralize the filtrate with N hydrochloric acid, add

an equal volume of the reagent, boil, and allow to stand 20 minutes. Cool, dilute with alcohol, and examine under an ultra-violet lamp.

The alkali metals, alkaline earths, cobalt, nickel, iron, chromium, manganese, silver, mercury, lead, cadmium, uranium, vanadium, copper, fluoride, and oxidizing agents do not interfere in the final test.

The test may also be carried out as a spot test. The reagent is prepared by soaking aluminum-free paper in the reagent and drying. To make the test simply apply 1 drop of the solution to be tested to the paper, and examine the spot under ultra-violet light. The test is sensitive to 0.1% of either aluminum or gallium. Zinc, magnesium, beryllium, thorium, and zirconium do not interfere, but cobalt, iron, chromium, and fluoride must be absent.

1. J. A. Radley, *Analyst* **68**, 369-70 (1943); *C.A.* **38**, 930 (1944).

### SOLWAY PURPLE

Synonym: 1-Hydroxy-4-*o*-sulfo-*p*-tolylaminoanthraquinone, sodium salt

$C_{21}H_{14}O_6NSNa$

Mol. Wt. 431.38

Color Index, 1073.

**Use:** Detection of boron.

Solway purple is obtained as a reddish-blue powder or paste. It dissolves in water to form a reddish-blue solution. It dissolves in sulfuric acid to form a bright blue solution.

**Preparation:** Solway purple is prepared by condensing quinalizarin with one molecular proportion of *p*-toluidine, and sulfonating the product.

**Detection of boron.** A solution of solway purple in concentrated sulfuric acid gives a deep blue color with small quantities of boron. In the absence of fluoride, this reaction is capable of detecting boron in 0.1 ml. of a solution containing 0.01 g. of borax in 1 liter of water.<sup>1</sup>

1. J. A. Radley, *Analyst* **69**, 47-8 (1944); *C.A.* **38**, 1973 (1944).

### TETRABROMOPHENOLPHTHALEIN

$C_{20}H_{10}O_4Br_4$

Mol. Wt. 633.94

Beil. Ref. XVIII, 149.

**Use:** Detection of copper and iron.

Tetrabromophenolphthalein is a white to slightly yellow powder which melts at 280-285° C. with decomposition. It is insoluble in water and only sparingly soluble in alcohol, but is soluble in ether and dissolves in alkalies with the formation of a violet color.

The sodium salt is a pale blue to purplish-blue powder, which decomposes on exposure to air. It is very soluble in water, but is only slightly soluble in alcohol and is insoluble in ether. It should be stored in a tightly closed container and protected from light.

**Preparation:** Dissolve 5 parts of phenolphthalein in 20 parts of boiling alcohol, and to the hot solution add 10 parts of bromine in 10 parts of glacial acetic acid. Tetrabromophenolphthalein crystallizes in colorless prisms on cooling. The product is purified by recrystallizing from alcohol or acetic acid.<sup>1,2</sup>

**Detection of copper and iron.** The violet-colored solution of the sodium salt of tetrabromophenolphthalein reacts with cupric and ferric ions to yield reddish-brown precipitates. By using a 0.2 per cent aqueous solution of the sodium salt, and carrying out the test on a spot plate, as little as 0.25γ of copper can be detected. Ferric iron gives a similar precipitate. Mercurous salts give a greenish-yellow precipitate and mercuric salts a yellowish-white precipitate.<sup>3</sup>

1. A. v. Baeyer, *Ber.* 9, 1231 (1876).

2. A. v. Baeyer, *Ann.* 202, 78 (1880).

3. E. A. Kocsis R. Horvai, *Mikrochemie ver. Mikrochim. Acta.* 29, 44-5 (1941); *C.A.* 35, 5412 (1941).

## TETRAMETHYL-*p*-DIAMINODIPHENYLMETHANE

Synonym: Tetra base, Arnold's base

$C_{17}H_{22}N_2$

Mol. Wt. 254.36

Beil. Ref. XXX, 239.



**Use:** Detection of ammonia, cerium, chlorine, copper, ferricyanide, gold, hypochlorite, lead, manganese, molybdenum, ozone, periodate, and vanadium.

Determination of copper, lead, manganese, and tungsten.

Tetramethyl-*p*-diaminodiphenylmethane consists of white to bluish-white, lustrous crystals. It sublimes without decomposition. It melts at 90-91° C. and boils at 390° C. It is insoluble in water, only slightly soluble in alcohol, but dissolves in benzene, ether, carbon disulfide and acids.

**Preparation:** Dissolve 40 g. of dimethylaniline in 100 ml. of alcohol and add 30 ml. of hydrochloric acid. Cool and add 12.5 ml. of 40 per cent formaldehyde solution and place the mixture in water. Allow the dark colored mixture to stand for 1-2 days and warm slightly, and then allow to cool. Pour into a concentrated solution of sodium acetate, which is kept cool with ice. The crude product separates in the form of plate-like crystals. Purify by recrystallizing from alcohol.<sup>1</sup>

**Detection of lead.** Tetramethyl-*p*-diaminodiphenylmethane is oxidized to a blue diphenylmethane dye by a number of substances, which may accordingly be detected by this reaction. The reagent may be used to detect or determine small quantities of many elements which have at least two relatively stable valence forms, and which have a higher oxide or hydroxide which is insoluble in the oxidizing solution.<sup>2</sup>

Small quantities of lead may be converted into lead dioxide, and the latter used to develop the blue color by the oxidation of tetramethyl-*p*-diaminodiphenyl-



methane.<sup>36</sup> This reaction was first reported by Trillat,<sup>3</sup> who used a solution of 5 g. of tetramethyl-*p*-diaminodiphenylmethane dissolved in 100 ml. of 10 per cent acetic acid. This solution should not develop a blue color when cold, nor when heated to boiling. It should be protected from light. When added to lead dioxide (and certain other oxidizing agents) this reagent produces an intense blue color, which permits the detection of small quantities of lead.

Carney<sup>4</sup> has pointed out that there are objections to the use of an acetic acid solution of the reagent for the detection of lead. Acetic acid solutions should be heated when used, and when heated the base immediately precipitates and does not dissolve until the solution is cooled. A colorless acetic acid solution of the reagent is also difficult to obtain. It is unstable and soon darkens on standing. The use of citric acid to eliminate these difficulties is recommended. The reagent is prepared as follows: Dissolve 2.5 g. of tetramethyl-*p*-diaminodiphenylmethane in a solution of 10 g. of citric acid in 10 ml. of water and dilute to 500 ml.

With any compound of lead, or manganese, in which the metal has a valence of more than two, a cold solution of the reagent produces a deep reddish-purple color due to the oxidation of the amine. Cobaltic and nickelic hydroxides also cause color formation, although the reaction takes place somewhat more slowly and the color is usually not so deep.

The following procedure for carrying out the lead test is described by Miller:<sup>5</sup>

**Procedure.** Separate the lead by precipitating as lead sulfide, dissolve in concentrated nitric acid, and then convert to the peroxide by oxidizing with bromine. Most interfering substances are removed by this treatment. Bismuth, however, must be separated by first precipitating the lead as sulfate. Filter the lead dioxide through glass wool or on a carefully hardened filter paper, after previously diluting the mixture. Suspend the lead dioxide in 5 ml. of concentrated hydrochloric acid, and warm with 1 ml. of a 0.1 per cent solution of the reagent in acetic acid. A bright blue color develops after about 5 minutes. The test is very sensitive and may be used to detect 0.001 mg. of lead in 10 ml. of solution.

Feigl and Neuber<sup>6</sup> have used tetramethyl-*p*-diaminodiphenylmethane for the detection of lead in the presence of bismuth, which interferes with the similar benzidine test. If not more than 11 times as much bismuth as lead is present, the test is satisfactory.

Jirkovsky<sup>7,8</sup> has used tetramethyl-*p*-diaminodiphenylmethane for the detection of lead in the determination of the purity of assay beads. The reagent may also be used for the confirmation of lead in schemes of qualitative analysis.<sup>37,38</sup>

**Determination of lead.** The blue color which is formed when small quantities of lead dioxide react with tetramethyl-*p*-diaminodiphenylmethane has been used for the colorimetric determination of small quantities of lead.<sup>9-14,48</sup> The method has been especially developed for the determination of lead in biological materials, but there appears to be no reason why it should not have other applications. The materials to which this determination has been applied consist essentially of urine, tissue, blood and feces.

**Procedure.** The weight of the sample taken varies according to the source of the material, which is decomposed with fuming nitric and sulfuric acids according to the usual methods. When the organic matter is completely decomposed, the resulting solution is evaporated to dryness and the residue dissolved in 50 ml. of water. To this solution add 1:3 ammonium hydroxide until faintly alkaline. This point is usually indicated by the precipitation of ferric hydroxide, but if sufficient iron is not present, *p*-nitrophenol may be used as the indicator. Add 0.1 g. of finely divided iron or aluminum, and pass hydrogen sulfide through the solution for 1 hour, and finally treat with hydrogen sulfide under pressure for 24 hours.

Filter on a Witt plate or through a very fine mat in a Gooch crucible. Wash the precipitate on the filter with a 3 per cent potassium cyanide solution to remove copper. (Caution: Remove the cyanide solution from the suction flask before proceeding!) Next wash the precipitate with a solution prepared by adding 3 ml. of concentrated sulfuric acid to 100 ml. of 50 per cent alcohol and passing hydrogen sulfide through the mixture for 1 hour. In this way iron, aluminum, manganese and calcium are removed, while lead remains behind as lead sulfide or lead sulfate. Traces of iron and aluminum may also be retained on the filter, but these do not interfere.

Dissolve the lead sulfide from the filter with 5 ml. of fuming nitric acid and evaporate just to dryness. Treat the filter with 5 ml. of 5 per cent sodium acetate solution to dissolve any lead sulfate, and add this to the dried residue from the lead nitrate solution, and then heat if necessary until all the solid has dissolved. Make the mixture neutral to litmus paper by adding either 1:10 sulfuric acid or 1:10 ammonium hydroxide, whichever may be required.

Place the mixture on a boiling water-bath, and add saturated bromine water until a permanent yellow color is obtained. Sodium persulfate or sodium hypochlorite may be used in place of bromine-water for the oxidation.

Heat the mixture for 2 hours and filter while hot through the same Gooch crucible which was used originally for collecting the lead precipitate. Before using, the Gooch crucible should be washed by filtering a few ml. of bromine water to remove any reducing agents which might be present. Wash the precipitate thoroughly to remove any residual bromine which is also capable of oxidizing the reagent.

Now dissolve the lead dioxide by filtering 25 ml. of a 1 per cent solution of tetramethyl-*p*-diaminodiphenylmethane in glacial acetic acid through the crucible, and collect the filtrate separately from all previous filtrates. The reagent should be added in small portions and each completely washed through before adding the next. The last portions filtered should come through the crucible colorless to indicate that all lead dioxide has been dissolved.

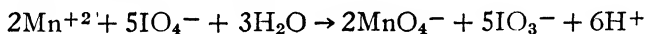
Finally determine lead by comparing the blue color of the acetic acid solution with that of a series of standards prepared by the action of known quantities of lead dioxide on the reagent.

**Detection of manganese.** Like lead dioxide, manganese dioxide is capable of oxidizing tetramethyl-*p*-diaminodiphenylmethane to an intensely blue col-

ored compound. This reaction was first used by Trillat<sup>3</sup> for the detection of small quantities of manganese. The reagent used by Trillat is prepared by dissolving 5 g. of tetramethyl-*p*-diaminodiphenylmethane in 100 ml. of 10 per cent acetic acid. This solution should not develop a blue color in the cold or when heated to boiling. It should be protected from light. When added to manganese dioxide, an intense blue color appears, which may be used for detecting small quantities of manganese.

Carney<sup>4</sup> has proposed the use of a solution in citric acid to overcome certain objections (see section on detection of lead) to the use of acetic acid solutions of tetramethyl-*p*-diaminodiphenylmethane. The reagent is prepared by dissolving 2.5 g. of the reagent in a solution of 10 g. of citric acid in 10 ml. of water and diluting to 500 ml. With any compound of manganese, in which the valence is greater than ~~two~~  $+2$ , a cold solution of this reagent gives a deep reddish-purple color due to the oxidation of tetramethyl-*p*-diaminodiphenylmethane.

Tillmans and Mildner<sup>15-17</sup> have applied Trillat's test to the detection of manganese in water. Manganese salts are oxidized to permanganates by warming with solutions of an alkali periodate:



Large quantities of manganese can be detected by the violet color of the permanganate ion, while small quantities can be made recognizable by adding a solution of tetramethyl-*p*-diaminodiphenylmethane in chloroform. An intense blue color is formed due to the oxidation of the reagent. In this reaction the permanganate is reduced to the manganous salt which is again oxidized by periodate; hence, in this test the manganese is detected as a result of its catalytic action.

**Procedure.** Shake 10 ml. of water to be tested with 0.1 g. of solid potassium periodate in a stoppered glass cylinder, and then acidify with 3 drops of acetic acid. Add slowly a few ml. of a freshly prepared 0.5 per cent solution of tetramethyl-*p*-diaminodiphenylmethane in chloroform. A blue color develops if manganese is present. By this reaction 0.05 mg. of manganese can be detected in 1 liter of water.

Chlorate, bromate, and iodate do not interfere with this test. Persulfate interferes by converting manganese salts to the higher oxides of manganese, which react with tetramethyl-*p*-diaminodiphenylmethane to give a blue color. Persulfate may be removed, however, by evaporating the sulfuric acid solution with a little silver nitrate. Colored salts must be absent. Chromium salts must be absent, since they are oxidized by periodate to chromate, which also oxidizes tetramethyl-*p*-diaminodiphenylmethane to give a blue color.

Feigl<sup>18</sup> has applied this reaction to a spot test for manganese:

**Procedure.** Place a drop of the solution to be tested on a spot plate and add a drop of a saturated solution of potassium periodate, a drop of 2 N acetic acid, and 2 drop of a 1 per cent solution of tetramethyl-*p*-diaminodiphenylmethane in chloroform. A blue color is formed with as little as 0.001% of manganese. The concentration limit of this reaction is 1:50,000,000.

Gutzeit<sup>19</sup> has used tetramethyl-*p*-diaminodiphenylmethane to detect manganese in minerals by a contact print process. A piece of gelatin-coated paper impregnated with a selective attacking agent is placed on the surface of a polished rock or mineral and pressed down tightly. After 2-5 minutes the paper is removed and treated with tetramethyl-*p*-diaminodiphenylmethane. A blue color appears with as little as 0.000001 mg. of manganese.

Dubsky and Langer<sup>20</sup> and Wenger and Duckert<sup>21</sup> have studied the various manganese reagents and report favorably on the use of tetramethyl-*p*-diaminodiphenylmethane.

The addition of an alcoholic solution of tetramethyl-*p*-diaminodiphenylmethane to a nearly neutral solution of manganous acetate produces a deep blue coloration. The character of this reaction is not known.

**Determination of manganese.** Harry<sup>22,23</sup> has used the reaction of manganese and tetramethyl-*p*-diaminodiphenylmethane (see, detection of manganese) for the colorimetric determination of small quantities of manganese.

**Reagents.** *Tetramethyl-*p*-diaminodiphenylmethane reagent:* Dissolve 0.5 g. of tetramethyl-*p*-diaminodiphenylmethane in 100 ml. of alcohol.

*Standard manganese solution:* Dissolve 0.158 g. of pure manganese dioxide in 10 ml. of concentrated hydrochloric acid and dilute to 1 liter. Each ml. contains 0.1 mg. of manganese.

**Procedure.** Dissolve the weighed sample in 1:1 hydrochloric acid, and dissolve the same weight of manganese-free iron wire with the sample. An equivalent amount of ferric chloride may be used instead of the iron wire. If manganese is to be determined in iron or steel, the addition of the wire or ferric chloride may be omitted. Add 0.5 ml. of concentrated nitric acid and evaporate to dryness. Heat until the oxides of nitrogen are expelled, and dissolve the residue in the smallest possible volume of 1:1 hydrochloric acid. Add 14 ml. of 1:1 sulfuric acid, and evaporate to the appearance of sulfur trioxide fumes. Add 10 ml. of 20 per cent sulfuric acid and boil, and when solution is complete, dilute to 250 ml. with boiling water.

Add 25 ml. of a 25 per cent solution of ammonium persulfate and heat to boiling for 15 minutes. Add an additional 25 ml. of persulfate solution and heat 15 minutes longer. Filter the precipitated manganese dioxide, and place the paper and precipitate in 10 ml. of concentrated hydrochloric acid and heat to boiling. Dilute to 200 ml. and filter into a 250-ml. flask. Dilute to the mark with distilled water.

Place 1 ml. of sample and 1 ml. of standard manganese solution in each of two 10-ml. flasks and dilute with distilled water to about 6 ml. To each add 1 ml. of a 0.5 per cent solution of tetramethyl-*p*-diaminodiphenylmethane and 1 ml. of glacial acetic acid. Mix and add 0.5 ml. of N sodium hydroxide solution. Again mix and add glacial acetic acid dropwise until color development reaches a maximum. Dilute to 10 ml. and compare.

If the color developed is too deep for comparison, or if a precipitate is formed, dilute both sample and standard and repeat the determination.

Wester<sup>24</sup> has used tetramethyl-*p*-diaminodiphenylmethane for the determination of manganese in plants.

**Detection of periodate.** Periodate may be detected by a reaction similar to that used for the detection of manganese (page 000), which is based on the oxidation of manganous salts to permanganates by warming with an alkali periodate in an acid solution. Small amounts of permanganate are detected with the aid of tetramethyl-*p*-diaminodiphenylmethane. Interference is the same as that described for the detection of manganese.<sup>45</sup>

**Reagent.** Mix equal volumes of a 2 N acetic acid solution saturated in the cold with tetramethyl-*p*-diaminodiphenylmethane and a 10 per cent manganous chloride solution. Prepare just before using.

**Procedure.** Mix 1 drop of the reagent with 1 drop of the test solution. A blue coloration is a positive test for periodate. In this way 0.5γ of periodate can be detected at a concentration limit of 1:100,000.

**Detection of vanadate and molybdate.** The addition of a solution of tetramethyl-*p*-diaminodiphenylmethane in acetic acid of pH 3.5 to a neutral solution containing a vanadate causes the immediate formation of a yellow precipitate which gradually turns green. This compound has the composition,  $(\text{VO}_3)_4\text{C}_{17}\text{H}_{22}\text{N}_2$ . This reaction has been used by Papafil and Cernatesco<sup>25,26</sup> for the detection of vanadates. The reaction is sensitive to about 0.05 g. of vanadate per liter of solution.

To detect molybdate proceed as follows:<sup>26</sup>

**Reagent.** Dissolve 1.5 g. of tetramethyl-*p*-diaminodiphenylmethane in 300 ml. of water containing 10 ml. of glacial acetic acid. Filter, add dilute ammonium hydroxide dropwise until a faint opalescence appears, and filter again.

**Procedure.** Add a little of the above reagent to a solution containing a molybdate. A blue precipitate is formed.

With tungstate, only an opalescence appears.

**Determination of tungsten.** Kafka<sup>27</sup> has used tetramethyl-*p*-diaminodiphenylmethane for the quantitative precipitation of tungstate.

**Reagent.** Treat 6 g. of tetramethyl-*p*-diaminodiphenylmethane with 4 ml. of concentrated hydrochloric acid and dilute with water to 100 ml.

**Procedure.** To 50 ml. of a solution of sodium tungstate, add with stirring 10 ml. of the reagent. A white precipitate separates and upon standing becomes blue. Allow to stand with occasional stirring for 0.5-1 hour and test the clear supernatant liquid for complete precipitation. Wash the precipitate with a solution of 5 ml. of the tetramethyl-*p*-diaminodiphenylmethane reagent in 100 ml. of solution. Ash wet in a platinum crucible and ignite to constant weight. Weigh as  $\text{WO}_3$ .

Papafil and Cernatesco<sup>25</sup> state that any excess ammonium salts must be

removed. They also recommend that the precipitate be dried at 110° C. and then ignited to the oxide.

**Detection of gold.** Tetramethyl-*p*-diaminodiphenylmethane reacts with very dilute solutions of gold chloride to yield a beautiful purple color. This soon changes to blue and eventually becomes colorless. The blue color reappears on warming. This reaction constitutes a very delicate test for gold.<sup>4</sup> There is no interference with this reaction by platinum or palladium. Free mineral acids interfere, but this may be eliminated by first neutralizing the solution to be tested and then making slightly acid with citric acid. For solutions containing only gold chloride, the sensitivity of the test is 0.01 mg. of gold in 50 ml. of solution.

**Detection of ammonia.** Carney<sup>4</sup> has used tetramethyl-*p*-diaminodiphenylmethane in an indirect test for ammonia. This test is based upon the fact that hydrogen peroxide is without affect upon a solution of a manganous salt unless the solution is slightly alkaline. In the presence of even a trace of alkali, the peroxide instantly oxidizes manganese to a brown higher oxide, and this in turn yields a blue color with tetramethyl-*p*-diaminodiphenylmethane:

**Procedure.** Heat the solution to be tested with sodium hydroxide and allow the vapor which forms to come in contact with a test paper prepared as follows: Moisten a strip of filter paper with a solution prepared by dissolving 2 g. of manganous sulfate in 200 ml. of water and adding 5 ml. of hydrogen peroxide. If ammonia is present in the gases striking the paper, a brown stain appears. When this stain is moistened with a drop of tetramethyl-*p*-diaminodiphenylmethane, a deep purple color is formed. With small quantities of ammonia no brown stain may appear, but the purple color may be observed when the reagent is added. This reaction is capable of detecting 0.02 mg. of ammonia.

**Detection of ozone and other oxidizing agents.** Arnold and Mentzel<sup>29-35</sup> and others<sup>28,32,34,35,39</sup> have used tetramethyl-*p*-diaminodiphenylmethane for the detection of ozone in water.

**Procedure.** To 1-2 ml. of a 2 per cent silver nitrate solution or a 10 per cent manganous sulfate solution, add 1-2 drops of a saturated solution of tetramethyl-*p*-diaminodiphenylmethane in a methyl alcohol, and then add 25-35 ml. of the water to be tested. A distinct blue coloration appears if ozone is present. This fades, however, after standing for some time.

The addition of ferrous sulfate to the silver or manganese solution is recommended to prevent interference by oxidizing substances, such as chlorine, bromine, and permanganate. Tetramethyl-*p*-diaminodiphenylmethane may also be used to detect ozone in mixtures containing hydrogen peroxide and the oxides of nitrogen.<sup>4,28-30</sup> This test is carried out by holding in the gas to be tested moist strips of filter paper impregnated with an alcoholic solution of the reagent. With ozone a violet color is obtained; with nitrogen dioxide, a straw-yellow color is formed; and there is no reaction with hydrogen peroxide. More recently Masterman<sup>82</sup> has studied the reaction of tetramethyl-*p*-diaminodiphenylmethane

with chlorine, ozone and hypochlorites. The addition of ozone to a solution of tetramethyl-*p*-diaminodiphenylmethane gives a series of colors ranging from violet through amethyst, rose and ruby red. The addition of chlorine to a solution of tetramethyl-*p*-diaminodiphenylmethane gives a series of colors ranging from blue through grass-green, olive-green, orange, yellow and finally a complete bleaching. Hypochlorites may give the same sequence as ozone with a concentrated solution of tetramethyl-*p*-diaminodiphenylmethane in ethyl alcohol.

Aqueous solutions of hypochlorites prepared electrolytically give chlorine and the ozone colors. Hypochlorites prepared by chemical methods do not give the same colors as ozone except on standing for some time, but the addition of sodium chloride assists in color formation. It is possible that electrolytically prepared products contain ozone.

**Detection of cerium.** Manelli<sup>44</sup> recommends the following sensitive test for cerium:

**Procedure.** Add a little sodium bismuthate to an acetic acid solution of the cerium salt, boil a few minutes, and filter. Place 1-2 drops of this mixture on a spot plate, and treat with a drop of a 1 per cent solution of tetramethyl-*p*-diaminodiphenylmethane in chloroform. A blue color indicates the presence of cerium.

If the original solution contains sulfuric acid, buffer with sodium acetate.

**Detection of ferricyanide.** Tetramethyl-*p*-diaminodiphenylmethane is recommended by Lapin<sup>41</sup> as a very sensitive reagent for ferricyanide. The test is based on the oxidizing action of the ferricyanide ion. In a weakly acid solution, 0.1% of ferricyanide can be detected. The reaction is somewhat less sensitive in neutral and alkaline solutions. All remaining cations and anions either do not interfere or cause a slight decrease in the sensitivity.

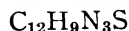
**Detection and determination of copper.** A reddish-violet precipitate is formed when an alcoholic solution of tetramethyl-*p*-diaminodiphenylmethane is added to a neutral solution containing cuprous ions. This reaction may be used to detect as little as one part of copper in 4,000,000 parts of solution. A large excess of the reagent must be avoided.<sup>42</sup> Muller and Burtzell<sup>40</sup> have studied this reaction as a possible method for the colorimetric determination of copper, but they report that the color fades rapidly.

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33. C. Arnold and C. Mentzel, *Z. anal. Chem.* **43**, 50 (1904).
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43. M. Fields, *New Zealand J. Sci. Tech.* **23B**, 224-6 (1942).
44. G. Mannelli, *Ann. chim. applicata.* **32**, 356-9 (1942); *C.A.* **38**, 4213 (1944).
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## THIONINE

Synonym: Base of Lauth's violet



Beil. Ref. XXVIII, 391.



Color Index, 920.

**Use:** Determination of tin.

Thionine consists of brownish-black leaves or greenish needles. It is very slightly soluble in hot water, and is slightly soluble in alcohol and ether with a yellow color. It is soluble in chloroform and benzene.

The chloride consists of gold-green crystals. It is moderately soluble in hot water with the formation of a violet colored solution. It dissolves in alcohol with a red to blue color.



**Preparation:** Thionine is prepared by the successive treatment of an acid solution of phenylenediamine hydrochloride with hydrogen sulfide and ferric chloride.<sup>1</sup>

**Determination of tin.** Leutwein<sup>2</sup> has suggested the substitution of Lauth's violet for methylene blue for the titration of stannous tin. Stannous salts in 4-6 N hydrochloric acid can be titrated with a solution of methylene blue or Lauth's violet in much the same manner as described for the titration of tri-valent titanium. The end-point is shown by a final blue color. One mole of methylene blue is equivalent to 1 mole of stannous chloride.

1. A. Koch, *Ber.* **12**, 2069 (1879).

2. F. Leutwein, *Z. anal. Chem.* **120**, 233-42 (1940); *C.A.* **35**, 1001 (1941).

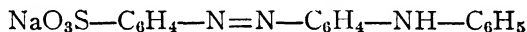
## TROPAEOLIN OO

Synonym: Diphenylamine orange, orange GS, orange N, orange IV, fast yellow, acid yellow D, and aniline yellow

$C_{18}H_{14}N_3O_3SNa$

Beil. Ref. XVI, (319). Color Index, 143.

Mol. Wt. 375.37



**Use:** Detection of zinc.

Determination of magnesium.

Tropaeolin OO is an orange-yellow powder which dissolves in alcohol and water with the formation of orange-yellow solutions. It is somewhat less soluble in ether and is insoluble in benzene.

**Preparation:** The dye is prepared by coupling diazotized sulfanilic acid with an alcoholic solution of diphenylamine in the presence of hydrochloric acid and then converting to the sodium salt.<sup>1</sup>

**Detection of zinc** Alkali ferricyanides oxidize tropaeolin OO and certain other organic compounds with a consequent change of color and the formation of ferrocyanides. Normally this oxidation proceeds very slowly, but if the ferrocyanide formed is removed by precipitation as insoluble zinc ferrocyanide the oxidation proceeds rapidly. This reaction has been used by Eegriwe<sup>2</sup> as a sensitive test for zinc. This test is particularly useful in a systematic scheme of analysis, since it may be carried out in the presence of chromium and aluminum after reducing the chromium with hydrogen peroxide.<sup>3</sup> A hydrochloric acid solution of the dye is red, but this color disappears when potassium ferricyanide and a little zinc are present.

**Reagent.** Dissolve 5-10 mg. of tropaeolin OO in 100 ml. of water.

**Procedure.** Mix one drop of the reagent with 3 drops of a 2 per cent solution of potassium ferricyanide and add hydrochloric acid until a red color

appears. Then add 1 drop of a weakly acidified zinc solution. The red color disappears within 5 minutes.

This test may be used to detect as little as 0.005 mg. of zinc.

**Determination of magnesium.** Tropaeolin OO forms with magnesium a very slightly soluble salt,  $(\text{O}_3\text{S}-\text{C}_6\text{H}_4-\text{N}=\text{N}-\text{C}_6\text{H}_4-\text{NH}-\text{C}_6\text{H}_5)_2\text{Mg}$ . This reaction has been used for the determination of magnesium. The following gravimetric method is recommended by Lang:<sup>5</sup>

**Procedure.** Heat the neutral, calcium-free solution to boiling, and precipitate magnesium with a saturated solution of tropaeolin OO. Add a quantity of tropaeolin OO such that the mixture when cold is orange-red in color. Cool, filter with suction on a glass filter crucible, and wash with water. Dry for 2 hours at 105° C., cool, and weigh. One mg. of the precipitate contains 0.033 mg. of magnesium.

Zahradnicek,<sup>4</sup> who originally proposed tropaeolin OO as a reagent for magnesium, based a colorimetric procedure on the fact that the color of a solution of the dye is weakened in the presence of magnesium, and in proportion to the quantity of magnesium present. More recently, Lang<sup>5</sup> has described the following method for the determination of magnesium in biological materials:

**Procedure.** Dilute 2 ml. of serum with 1 ml. of water, and add 1 ml. of saturated ammonium oxalate solution. Allow to stand 1 hour and centrifuge off the precipitated calcium oxalate. Transfer 3 ml. of the centrifugate to a 10-ml. volumetric flask, and add 2 ml. of 10 per cent sodium tungstate and 2 ml. 0.67 N sulfuric acid. Dilute to the mark and mix well. Filter or centrifuge, and transfer 4 ml. of the clear filtrate to a 10-ml. centrifuge tube, which is placed in boiling water. To the tube add 2 ml. of a freshly filtered, saturated solution of tropaeolin OO. Cool in ice water, allow to stand 1 hour, centrifuge, and wash the precipitate with 4-ml. portions of water until the washings are only slightly colored. This usually requires about 4 washings. Dissolve the precipitate in 4 ml. of concentrated sulfuric acid with stirring, transfer the red-violet solution to a 50-ml. flask, wash with water to make the transfer quantitative, and then dilute to the mark. Measure the color with a step photometer with a filter S53 or in a colorimeter. Use 1 ml. of a 0.001 N magnesium solution (= 12.2γ Mg) for preparing the standard. The quantity of magnesium corresponds to that in 0.6 ml. of serum.

This method may be used for 1-2γ of magnesium per ml. with an error of about 5 per cent.

According to Havinga,<sup>6</sup> the magnesium precipitate dissolves in water to the extent of  $3.25 \times 10^{-4}$  mg. per ml. at 20° C. Excessive washing should be avoided, and better results are obtained by using an aliquot of the solution rather than the washed precipitate. To do this, precipitate magnesium in a centrifuge tube as described above, but using a measured excess of the tropaeolin solution. Centrifuge, remove an aliquot of the clear supernatant liquid, and treat the aliquot with sulfuric acid. Determine the excess tropaeolin with a Pulfrich photometer.

As little as 0.0001 mg. of magnesium can be determined satisfactorily by this method.

1. R. Meyer, *Ber.* **53**, 1273 (1920).
2. E. Eegriwe, *Z. anal. Chem.* **74**, 225-31 (1928); *C.A.* **22**, 3859 (1928).
3. B. Tougarinoff, *Ann. Soc. Sci. Bruxelles.* **50**, Ser. B, 145-246 (1930); *C.A.* **25**, 1456 (1931).
4. J. Zahradnick, *Biochem. Z.* **191**, 61-73 (1927); *C.A.* **22**, 1607 (1928).
5. K. Lang, *Biochem. Z.* **253**, 215-17 (1932); *C.A.* **27**, 116 (1933).
6. E. Havinga and A. F. K. Buys Ballot, *Rec. trav. chim.* **61**, 849-54 (1942); *C.A.* **38**, 5467 (1944).

## TRYPAFLAVINE

Synonym: Acriflavine, flavine, 2,8-diamino-10-methochloride-acridine monohydrochloride

$C_{14}H_{14}N_3Cl \cdot HCl$

Mol. Wt. 296.18

Color Index, 790.

**Use:** Detection of oxygen and rhenium.

Trypaflavine hydrochloride consists of brownish-red, odorless granules or powder. It is soluble in about five parts of water, incompletely soluble in alcohol, and almost insoluble in chloroform and ether.

**Detection of oxygen.** Kaustky and Hirsch<sup>1</sup> have used trypaflavine for the detection of traces of oxygen. Oxygen can be detected at pressures as low as 0.0005 mm. of mercury by its action in destroying the phosphorescence of trypaflavine adsorbates. As adsorbents, well aged gels of highly polymerized inorganic acids such as silicic acid, or hydroxides, such as aluminum hydroxide are suitable.

The adsorbent must be neither opaque or colored.

**Detection of rhenium.** Geilmann and Wrigge<sup>2</sup> have suggested the use of trypaflavine for the microdetection of rhenium.  $H_2ReCl_6$  yields crystals with trypaflavine which can be recognized under the microscope.

1. H. Kautsky and A. Hirsch, *Z. anorg. allgem. Chem.* **222**, 126-34 (1935); *C.A.* **29**, 4288 (1935).
2. W. Geilmann and F. W. Wrigge, *Z. anorg. allgem. Chem.* **231**, 66-77 (1937); *C.A.* **31**, 3415 (1937).

## TRYPAN RED

$C_{82}H_{19}N_6O_{16}S_5Na_5$

Mol. Wt. 1002.77

Color Index, 438.

**Use:** Detection of bromide, chloride and nitrite.

Trypan red is a brown powder which dissolves in water to form a red solution.

**Preparation:** The dye is prepared by coupling tetrazotized benzidine-3-sulfonic acid with two molar proportions of  $\beta$ -naphthylamine-3,6-disulfonic acid.

**Detection of nitrite.** The dye trypan red has been used by Percs<sup>1</sup> as a sensitive reagent for nitrite. Nitrite is detected in the presence of nitrate by the following method:

**Procedure.** Neutralize the solution to be tested, and to 5 ml. of this solution add 5 drops of 5.0 N sulfuric acid and one drop of 0.1 per cent aqueous solution of trypan red.

In the presence of more than 0.005 mg. of nitrite ion, the orange-red solution changes to violet within 10 minutes.

**Detection of chloride and bromide.** Chlorides and bromides may be detected by means of a color reaction with trypan red.

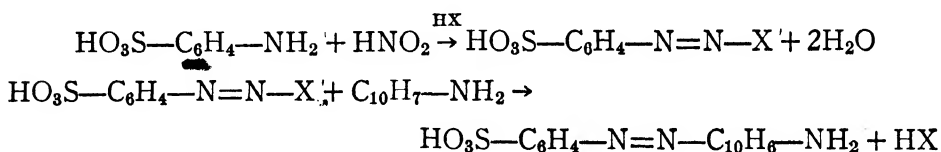
**Procedure.** Add 5 drops of 5 N sulfuric acid to 5 ml. of neutral solution to be tested, and treat with 1 ml. of 3 per cent hydrogen peroxide. Then add 1 drop of 0.1 per cent trypan red solution. A lemon-yellow color appears within 10 minutes if more than 0.1 mg. of chloride or more than 0.03 mg. of bromide is present.

1. E. Percs, *Ber ungar. pharm. Ges.* **14**, 30-1 (1938); *C.A.* **32**, 3293 (1938).

## CHAPTER XVII

### DYES USED IN THE DETECTION OF NITRITE

One of the oldest and best known of the nitrite tests is based on the formation of diazo compounds by the action of nitrous acid on primary aromatic amines, followed by coupling with suitable aromatic compounds to form intensely colored dyes. Typical of these reactions is that with sulfanilic acid and  $\alpha$ -naphthylamine.



This reaction was first used for the detection of nitrites and nitrous acid by Griess,<sup>1</sup> Ilosvay,<sup>2</sup> Lunge and Lwoff,<sup>3</sup> and Tschirikow.<sup>4</sup>

A great many dyes and many coupling agents have been used with varying results, although many of the compounds studied serve as sensitive reagents for nitrous acid. Dubsky and Okac<sup>5,6</sup> have carefully studied the use of a number of these dyes with various coupling compounds, and have reported their results in Tables 67 and 68. Many modifications of the Griess reaction have been proposed by different investigators, although for the sake of uniformity in tabulating the results obtained with different dyes, the following procedure has been recommended:

**Procedure.** To 2 ml. of the nitrite solution, add dropwise sufficient dye solution (10-50 mg. per 100 ml.) to impart a perceptible color to the solution (1-5 drops). Then add 1 ml. of hydrochloric acid and after 10 minutes add a small crystal of the coupling agent, and then make solution alkaline with concentrated ammonium or sodium hydroxide.

TABLE 67.

The following abbreviations are used in the following table:

c = colorless; y = yellow; br = brown; o = orange; r = red; v = violet; b = blue.

Numbers following the letters indicating color (e.g., y-6) signifies that the solution was yellow when  $10^{-6}$  g. of  $\text{HNO}_3$  was present.

	Color of Reagent Solution	Color with $\text{HNO}_3$	Coupling Compound		
			Phenol	$\alpha$ -Naphthol	$\alpha$ -Naphthylamine
Benzidine	c	y-6	y	r-7	v-7
2-Aminoanthraquinone	y	c	r-6	b-6	..
$\alpha$ -Naphthol	c	y-7	..	..	..
Fuchsin I	r	y	y-7	r-7	v-8
Chrysaniline	y	y	..	r-7	r-7
Phosphine E	y	y	o-5	r-7	r-7
Primuline	y	y	o-7	r-7	r-6
Aminoazobenzene	y	y	o-6	r-7	r-6
Spirit yellow	y	y	o-6	r-7	..
True yellow S	y	c	o-6	b-7	r-7
Direct black HB	rv	b-6	r-7	..	b-7
Diamine true blue	b	b	r-6	..	b
Nako B	br	y-5	y-5	o-6	v-6
Nako D	br	br	b	v	br
Victoria violet 4BS	v	v	r-6	b-6	v
Rhodamin 3G extra	r	c	b-6	..	b-7

TABLE 68.—COUPLING COMPOUNDS USED

1. Phenol	10. $\beta$ -Naphthol	18. 2-Naphthylamine-3,6-disulfonic acid
2. Salicylic acid	11. R-Salt	19. 2-Amino-5-naphthol-7-sulfonic acid
3. Resorcinol	12. Chromotropic acid	20. 1-Amino-5-naphthol-7-sulfonic acid
4. Metanilic acid	13. $\alpha$ -Naphthylamine	21. 1-Amino-8-naphthol-3-sulfonic acid
5. m-Aminophenol	14. $\alpha$ -Naphthylamine-sulfonic acid	22. 1-Amino-8-naphthol-3,6-disulfonic acid
6. $\alpha$ -Naphthol	15. 2-Naphthylamine-5-sulfonic acid	23. 1-Amino-8-naphthol-4,6-disulfonic acid
7. 1-Naphthylamine-5-sulfonic acid	16. $\beta$ -Naphthylamine	
8. 1-Naphthol-5-sulfonic acid	17. 2-Amino-8-naphthol-6-sulfonic acid	
9. 1-Naphthol-3,8-disulfonic acid		

Abbreviations used:

c. = colorless  
y. = yellow  
or. = orange

br. = brown  
r. = red  
gn. = green

v. = violet  
bl. = blue  
gr. = gray

The concentration given ( $10^{-6}$ , etc.) refers to the sensitivity of the reaction. Thus,  $10^{-6}$  indicates that nitrite may be detected at a concentration of  $1:10^6$ . When alkali hydroxides are used instead of  $\text{NH}_4\text{OH}$  the number of the coupling reagent is enclosed in parenthesis. (Thus, (1.) means that an alkali hydroxide was used for the coupling reaction when phenol was the coupling reagent.) The expression  $>10^{-5}$  signifies that the sensitivity of the reaction is greater than  $1:10^5$  (for example,  $1:2 \times 10^5$ ,  $1:3 \times 10^5$ , etc.).



TABLE 68.—Continued

Dye	Color of Solution	Color with $\text{HNO}_3$	Coupling Agent	
H-acid (Kb) .....	c.	c.	1. r. 6. r.	13. r. 23. r.
1-Aminoanthraquinone (B) .....	y.or	c.10 <sup>-5</sup>		
2-Aminoanthraquinone (B) .....	y.	c.10 <sup>-5</sup>		
$\alpha$ -Naphthol .....	c.	y.<10 <sup>-7</sup>	(1.) r. (6.) bl.	>10 <sup>-6</sup> >10 <sup>-6</sup>
Thiodiphenylamine .....	gr.	y.br.10 <sup>-6</sup>		
Fuchsin I (Gr.-E.) .....	r.	y.	1. y. 2. y. 3. y. 5. y. 6. r. 8. r. 9. r. 10. r.	11. r. 12. r. 13. v. 14. r. 15. y. 16. v. 22. r.
Rosanilinehydrochloride (Kb)	r.	y.	1. y. 5. y. 6. r. 1. y. 6. r. 1. y. 5. y. 6. r. 1. y. 6. r.	>10 <sup>-6</sup> >10 <sup>-6</sup> >10 <sup>-6</sup> >10 <sup>-6</sup> 10 <sup>-7</sup> 10 <sup>-6</sup> 10 <sup>-6</sup> 10 <sup>-6</sup> 10 <sup>-6</sup> 10 <sup>-6</sup>
Newfuchsin 90 (Gr.-E) .....	r.	y.	1. y. 5. y. 6. r. 1. y. 6. r.	>10 <sup>-6</sup> >10 <sup>-6</sup> >10 <sup>-6</sup> >10 <sup>-6</sup> 10 <sup>-7</sup>
Pararosaniline (Kb) .....	r.	y.	1. y. 5. y. 6. r. 1. y. 6. r.	>10 <sup>-6</sup> >10 <sup>-6</sup> >10 <sup>-6</sup> >10 <sup>-6</sup> 10 <sup>-7</sup>
Acid fuchsin (Kb) .....	r.	c.	1. y. 6. r.	13. r.v. 22. r.
Acid fuchsin B (M) .....	r.	c.	1. y. 6. r.	13. r.
Acid fuchsin G (M) .....	r.	c.	1. y. 6. r.	13. r.
Acid fuchsin O (M) .....	r.	c.	1. y. 6. r.	6. r. 9. r.or.





TABLE 68.—Continued

Dye	Color of Solution	Color with HNO <sub>3</sub>	Coupling Agent		
Aminazobenzene (H) .....	y.	y.	1. r.or. 6. r.v. 13. r.or.	>10 <sup>-6</sup> >10 <sup>-6</sup> 10 <sup>-6</sup>	22. r. 23. r. >10 <sup>-6</sup>
Spirit yellow R (K) .....	y.	y.	(1.) y. (3.) r.	>10 <sup>-6</sup>	(6.) r. (9.) r.
Fast yellow S (C) .....	y.	c.	(1.) or. (3.) r.v. (6.) bl. (9.) bl.	10 <sup>-6</sup> 10 <sup>-7</sup> >10 <sup>-6</sup>	(10.) v.r. 13. r. (12.) v. (22.) bl. >10 <sup>-6</sup>
Fast yellow O (M) .....	y.	c.	(1.) y. (3.) r. (5.) r.or. (6.) r.v.	>10 <sup>-6</sup> >10 <sup>-7</sup> 10 <sup>-7</sup>	(9.) r.v. 13. r. (22.) r.v. 10 <sup>-7</sup>
Fast yellow extra (B) .....	y.	y.	(5.) r. (6.) y.	10 <sup>-6</sup>	(9.) y.or. (12.) or.r.
Safranine (Dr. Grubler) .....	r.	bl.10 <sup>-6</sup>	(1.) bl.v. (6.) r. (9.) bl.v. (10.) bl.		13. bl.v. 16. bl. (22.) r.
Phenosafranine (M) .....	r.	bl.10 <sup>-6</sup>	1. r.v. 5. bl.v. 6. bl.v.	10 <sup>-6</sup>	13. bl.v. 22. r.
Rhodulin red B (By) .....	r.	bl.10 <sup>-6</sup>	(1.) r. (5.) r. (6.) r.v.		13. bl. (22.) r.
Rhodulin violet (By) .....	r.	bl.10 <sup>-6</sup>	6. y. 13. bl.	10 <sup>-7</sup>	14. r. 20. y.
Tannin heliotrope (C) .....	r.	bl.10 <sup>-6</sup>	(6.) gr.bl. (9.) b.gr. 13. bl.	>10 <sup>-7</sup>	16. bl. (22.) gr.bl.





TABLE 68.—Continued

Dye	Color of Solution	Color with HNO <sub>2</sub>	Coupling Agent	
Acid violet 4RS (M) .....	r.	c.10 <sup>-8</sup>	1. y. 6. y. 1. c.	10 <sup>-8</sup> 10 <sup>-8</sup> 10 <sup>-8</sup>
Methyl blue O (K) .....	bl.	c.	(1.) r. (6.) r.or.	10 <sup>-8</sup> 10 <sup>-8</sup>
Pure blue BSJ (J) .....	bl.	c.	(6.) r.or.	10 <sup>-8</sup>
Ice black DMO (Ki) .....	r.	r.	(6.) r.or.	10 <sup>-8</sup>
Diamine catechu (c) .....	r.	y.10 <sup>-8</sup>		
Rosanthere violet 5 R (J) .....	r.or.	r.		
Cresyl blue 2RN (L) .....	bl.	r.10 <sup>-8</sup>		
Cloth fast blue B (J) .....	v.bl.	y.		
Cloth fast blue GTB (J) .....	bl.	y.		
Cloth fast black B (J) .....	bl.	y.		
Naphthylamine black 10B (By) ..	bl.	v.bl.		
Amine black 10 BO (M) .....	bl.	v.bl.		
Agalma black 10B (B) .....	bl.	v.bl.		
Naphthol blue black S (C) .....	bl.	v.bl.		
Blue black NB (K) .....	bl.	v.bl.		
Naphthylamine black D (C) .....	v.	y.		
Tolyl black B (M) .....	bl.	y.		

A brief discussion of the dyes listed in the above tables is given below. Included in this list also are a few amino compounds used for nitrite detection which have not been described elsewhere.

	Color of Dye	Color with HNO <sub>3</sub>
Tolyl black BB (M) .....	bl.	y.
Sulfocyanine black B (By) .....	bl.	y.
Sulfocyanine black 2 B (By) .....	bl.	y.
Jet black R (By) .....	bl.v.	y.or.
Sulfocyanine G, GR extra, 3 R (By) .....	bl.	y.
Sulfocyanine 5 R (By) .....	v.bl.	y.
Tolyl blue GR extra (M) .....	bl.v.	y.
Tolyl blue 5 R extra (M) .....	bl.v.	y.
Sulfon black R (By) .....	bl.v.	y.br.
Acid black ZH (J) .....	bl.	v.bl.
Naphthochromcyanin R (J) .....	r.	light r.
Sulfo acid blue G (By) .....	bl.	y.br.
Sulfo acid blue R (By) .....	bl.	y.br.
Poirier blue .....	bl.	c.
Night blue (k) .....	bl.v.	bl.
Water blue 3 B (K) .....	bl.	c.

1. P. Griess, *Ber.* 12, 427 (1879).
2. L. Ilosvay, *Bull. soc. chim.* 3, 2, 317 (1889).
3. G. Lunge and A. Lwoff, *Bull. soc. chim.* 12, 345 (1894).
4. Tschirikow, *Pharm. Z. Russland.* 30, 802 (1891).
5. J. V. Dubsky and A. Okac, *Rec. trav. chim.* 46, 296-302 (1927); *C.A.* 21, 2627 (1927).
6. J. V. Dubsky and A. Okac, *Z. anal. Chem.* 75, 92 (1928).

### ACID BLACK ZH

Acid black ZH is an acid azo dye.

### ACID FUCHSIN B

Synonym: Acid fuchsin O, acid fuchsin G, acid magenta, rubine S, fuchsin S

Acid fuchsin B (Color Index, 692) is a mixture of the sodium or ammonium salts of di- and trisulfonic acids of rosaniline and pararosaniline.

### ACID VIOLET 4RS

Acid violet 4RS (Color Index, 692) is a mixture of magenta with acid violet.

### AGALMA BLACK 10B(B)

Synonym: Naphthol blue black



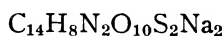
Color Index, 246.

The dye is a brown powder, soluble in water with a bluish-black solution, moderately soluble in alcohol, and soluble in sulfuric acid with a green solution.

**Preparation:** Add a neutral solution of 3.2 g. of 1-amino-8-naphthol-3,6-disulfonic acid to 1.4 g. of *p*-nitroaniline which has been diazotized in the usual manner. The mixture must remain strongly acid. Make faintly alkaline with sodium carbonate and add a solution obtained by the diazotization of 1 g. of aniline. Be sure that the solution remains alkaline. Salt out dye.

## ALIZARIN SAPHIROL B

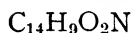
Alizarin saphirol B is an anthraquinone dye prepared by sulfonating 1,5-dihydroxyanthraquinone with 20 per cent fuming sulfuric acid at 100-120° C., followed by nitration of the product and subsequent reduction.



Color Index, 1054.

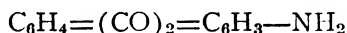
The dye is a greenish-black powder. It dissolves in water with a blue solution.

## 1-AMINOANTHRAQUINONE



Mol. Wt. 223.22

Beil. Ref. XIV, 177.



1-Aminoanthraquinone occurs in the form of red needles. Its melting point is 242-43°. It sublimes. The compound is insoluble in water, but is easily soluble in alcohol, ether, benzene, acetic acid, and is moderately soluble in hydrochloric acid.

**Preparation:** The compound is prepared by the reduction of 1-nitroanthraquinone with ammonium sulfide<sup>1</sup> or with sodium sulfide.<sup>2</sup>

1. Roemer, *Ber.* 15, 1790 (1882).

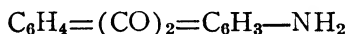
2. C. Graebe and S. Blumenfeld, *Ber.* 30, 1116-17 (1897).

## 2-AMINOANTHRAQUINONE



Mol. Wt. 223.22

Beil. Ref., XIV, 191.



This compound is obtained as red needles from alcohol. It melts at 302° C. It is insoluble in water, ether, and alkalies, but is soluble in alcohol and benzene. The solutions do not fluoresce.

**Preparation:** The reagent is prepared by heating 2 g. of 2-anthraquinone sulfonic acid with 25 ml. of 25 per cent ammonia to 190° C. for 5 hours.<sup>1</sup> The compound may also be obtained by the reduction of 2-nitroanthraquinone.<sup>2</sup>

1. H. R. Perger, *Ber.* 12, 1567 (1879).

2. A. Kliegl, *Ber.* 38, 295 (1905).

***p*-AMINOAZOBENZENE**

Synonym: Aniline yellow, spirit yellow



Beil. Ref. XVI, 307. Color Index, 15.

Mol. Wt. 197.23

**Use:** Detection of nitrite.

*p*-Aminoazobenzene is a yellow crystalline solid melting at 125-26° C. It is slightly soluble in hot water.

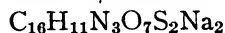
**Preparation:** Mix 10 g. of finely powdered diazoaminobenzene with 25 g. of aniline and 5 g. of aniline hydrochloride, and heat the mixture at 40° C. for one hour. Allow to stand at room temperature for 24 hours and add a slight excess of moderately concentrated hydrochloric acid. While adding the acid be careful that no great evolution of heat occurs. On cooling, *p*-aminoazobenzene separates along with aniline hydrochloride as a crystalline solid. Filter and wash with cold, very dilute hydrochloric acid. The violet crystals of *p*-aminoazobenzene hydrochloride remain on the filter. To convert to the free base, warm the hydrochloride with dilute ammonium hydroxide. Filter off the brown colored base and dissolve in hot ethyl alcohol to which is added a few drops of concentrated ammonium hydroxide.<sup>1</sup>

**Detection of nitrite.** An acid solution of *p*-aminoazobenzene is orange in color, while a basic solution is light yellow. When *p*-aminoazobenzene is diazotized by adding to a solution containing nitrite, no color change occurs, but upon coupling with  $\alpha$ -naphthol in an ammoniacal solution, an intense red-violet color appears. This reaction is sensitive to one part of nitrite in one million parts of solution.<sup>2,3</sup>

1. W. Staedel and H. Bauer, *Ber.* **19**, 1953 (1886).
2. J. V. Dubsky and A. Okac, *Rec. trav. chim.* **46**, 296 (1927).
3. J. V. Dubsky and A. Okac, *Z. anal. Chem.* **75**, 92 (1928).

**AMINO BLACK 10 BO(M)**

Same as Agalma Black 10 B(B).

**AZO ORSEILLE R(A)**

Color Index, 34.

Azo Orseille R(A) is prepared by coupling benzenediazonium chloride with an alkaline solution of 2-amino-8-naphthol-3,6-disulfonic acid.

The dye occurs as a red-brown powder. It dissolves in water and alcohol to form a yellowish-red solution.

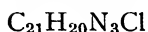


**BENZOCYANINE B**

Color Index, 476.

The dye is a bluish-gray powder which dissolves in water to form a blue solution. Its sulfuric acid solution is bluish-green in color.

**Preparation:** Couple tetrazotized tolidine with one mole of 1-amino-8-naphthol-3,6-disulfonic acid in an alkaline solution, and with one mole of 1-amino-8-naphthol-4-sulfonic acid, also in an alkaline medium.

**BENZOFLAVINE (Gr-E)**

Color Index, 791.

Benzoflavine (Gr-E) is an acridine dye.

The dye is prepared according to the method of Meyer and Gross.<sup>1</sup> It is a brownish-orange powder. It dissolves in water to form a yellow solution with a yellowish-green fluorescence, and in alcohol with a reddish-yellow solution with a strong greenish-yellow fluorescence.

1. Meyer and Gross, *Ber.* 32, 2352 (1899).

**BENZO RED-BLUE G**

Color Index, 473.

Benzo red-blue G is prepared by coupling tetrazotized tolidine with one mole of  $\alpha$ -naphthol-3,8-disulfonic acid and with one mole of 1-amino-8-naphthol-4-sulfonic acid in an alkaline solution.

The compound is a blue powder, soluble in water with a pure blue solution. It is insoluble in alcohol.

**BLUE BLACK NB(K)**

Same as Agalma Black 10B(B).

**CHICAGO BLUE B**

Color Index, 516.

Chicago blue B is prepared by coupling tetrazotized dianisidine with two moles of 1-amino-8-naphthol-4-sulfonic acid in an alkaline solution.

The dye is a blue powder, which dissolves in water, alcohol, and sodium hydroxide with the formation of blue solutions.

**CHICAGO BLUE R**

Color Index, 474.

Chicago blue R is prepared by coupling tetrazotized tolidine with two moles of 1-amino-8-naphthol-4-sulfonic acid in an alkaline solution.

The dye is a blue powder. It dissolves in alcohol with a blue solution, and in water with a violet-blue solution.

### CHRYSANILINE

Chrysaniline (Color Index, 793), is a mixture of the nitrates of *unsym*-diaminophenylacridine prepared by the condensation of *p*-aminobenzaldehyde with *m*-aminodiphenylamine, followed by oxidation of the resulting product.

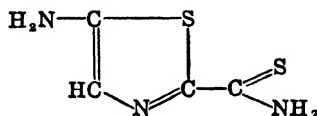
The dye is an orange-yellow powder. It dissolves in water, alcohol, and in sulfuric acid to form reddish-yellow solutions, which possess a green fluorescence.

### CHRYSEAN

$C_4H_5N_3S_2$

Mol. Wt. 159.14

Beil. Ref. XXVII, 334.



**Use:** Detection of nitrite.

Chrysean is obtained as yellow needles by crystallization from water. The compound is only slightly soluble in cold water, but is easily soluble in hot water. It is also soluble in alcohol, ether, acids, and alkalis. The melting point is 208-209° C.

**Preparation:** Chrysean is prepared by saturating a hot, saturated solution of potassium cyanide with hydrogen sulfide. The compound separates as yellow needles, which may be purified by recrystallization from hot water.<sup>1</sup>

**Detection of nitrite.** A cold, saturated alcoholic solution of chrysean reacts with a slightly acid solution of a nitrite to give a dark, reddish-brown precipitate. Since nitrates (if not too concentrated) cause only a red or yellow-red coloration with chrysean, this reagent may be used to detect nitrites in the presence of nitrates. Nitrite can be detected in the presence of nitrate by the following procedure:<sup>2-4</sup>

**Procedure.** Add a saturated alcoholic solution of the reagent to the solution to be tested, and carefully acidify with dilute hydrochloric acid. A reddish-brown precipitate forms if nitrite is present.

0.25γ of nitrite can be detected by this reaction at a dilution of 1:2,000,000.

The reaction is specific for nitrite only when cations of the hydrogen sulfide group are absent. A large amount of nitric acid causes a yellowish-red or red coloration, but if the concentration of nitrate does not exceed 2 N, the nitrite test is not affected.

The reaction of chrysean with nitrous acid depends upon the diazotization of one molecule of the amine reagent, and coupling with a second molecule of the reagent in an acid solution.

**Separation of nitrite and nitrate.** If an excess of chrysean is used in the nitrite precipitation, the precipitate contains all of the nitrite originally present in the solution, and since the precipitate is easily filterable, the reaction affords a convenient method for separating nitrite and nitrate.

**Procedure.** To the solution to be analyzed, add a saturated alcoholic solution of chrysean in moderate excess and carefully acidify with hydrochloric acid. Shake well, and, after separation of the precipitate, warm and filter. The filtrate must be yellow to show an excess of the reagent. No trace of nitrite remains in the filtrate, which may be tested for nitrate.

1. O. Wallach, *Ber.* **7**, 902 (1874).
2. J. V. Dubsky, J. Trtilek, and A. Okac, *Mikrochemie* **15**, 99-106 (1934); *C.A.* **28**, 6392 (1934).
3. J. V. Dubsky, A. Okac, B. Okac, and J. Trtilek, *Chem. Obzor.* **9**, 173-4, 189-91 (1934); *C.A.* **29**, 2875 (1934).
4. J. V. Dubsky, A. Okac, B. Okac, and J. Trtilek, *Z. anal. Chem.* **98**, 184-93 (1934); *C.A.* **29**, 2111 (1935).

### CLOTH FAST BLACK B

Synonym: Toly Black B, Toly Black BB(M), Sulfon cyanine Black B and 2B



Color Index, 307.

Cloth fast black B is a brownish-black powder. It dissolves in water with the formation of a violet solution, and in alcohol with a bluish-green solution.

### CLOTH FAST BLUE B

Synonym: Sulfon cyanine, Toly blue 5R extra, Toly blue GR extra

Cloth fast blue B (Color Index, 289) is a brownish-violet powder, which dissolves in water with a violet solution. It is not a pure compound.

### CLOTH FAST BLUE GTB(J)

Same as Cloth Fast Blue B.

### CRESYL BLUE 2RN

Cresyl blue 2RN (Color Index, 877) is an oxazine dye. It is prepared in a general way by the action of nitrosodialkyl-*m*-amino-*p*-cresol on *m*-diamines. The dye, formed from nitrosodiethyl-*m*-amino-*p*-cresol with *m*-phenylenediamine, is a green powder, soluble in water with a blue solution.

### DELTA PURPURIN 5B

Delta purpurin 5B is a dye obtained by coupling tetrazotized tolidine with two moles of crude  $\beta$ -naphthylamine-7-sulfonic acid. It is a mixture of 50 per

cent diamine red B, 25 per cent diamine red 3B (Color Index, 452), and 25 per cent benzopurpurin B (Color Index, 450).

The dye is a reddish-brown powder. Its aqueous solution is a bright yellowish-red color.

### DIAMINE BLACK BH

Same as direct black.

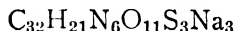
### DIAMINE CATECHU

Diamine catechu is an azo dye.

### DIAZO BLACK BHN

Same as direct black.

### DIRECT BLACK H.B.



Color Index, 401.

The dye is a grayish-blue powder. It dissolves in water with a reddish-blue solution, in hydrochloric acid with a violet solution, in sodium hydroxide with a reddish-violet solution, and in sulfuric acid with a blue solution.

**Preparation:** Tetrazotize 18.4 g. of benzidine and make the solution alkaline with sodium carbonate. Add a solution of 36 g. of 1-amino-8-naphthol-3,6-disulfonic acid (sodium salt) slowly, and then immediately add a solution of 2.5 g. of 2-amino-8-naphthol-6-sulfonic acid (sodium salt). After several hours, boil the mixture and salt out.

### EBOLI BLUE 2B



Color Index, 475.

This dye is a grayish-blue powder. It dissolves in water with a blue solution, and in sodium hydroxide with a reddish-violet solution.

**Preparation:** Tetrazotize tolidine and couple the resulting compound with 1-amino-8-naphthol-3,5-disulfonic acid in a solution kept alkaline with sodium carbonate. Stir for several hours until a sample dissolved in water gives a pure blue color on filter paper. Then heat, and salt out while hot.

### FAST YELLOW EXTRA B

Same as Fast Yellow B.

### FAST YELLOW O

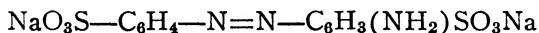
Same as Fast Yellow S.

**FAST YELLOW S**

Synonym: Fast yellow O, fast yellow extra B, acid yellow



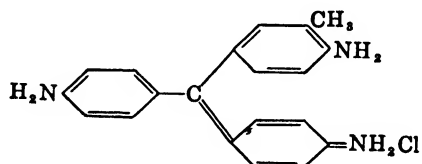
Color Index, 16.



**Preparation:** Stir one part of dry aminoazobenzene hydrochloride with 4-4.5 parts of fuming sulfuric acid (25 per cent  $\text{SO}_3$ ) at  $40^\circ\text{C}$ . until the product dissolves completely in dilute ammonia. Pour the mixture into 100 parts of dilute brine (d. = 1.06), filter, wash with brine, and convert to the sodium salt by dissolving in sodium carbonate and evaporating the solution to dryness below  $90^\circ\text{C}$ .

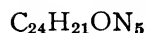
**FUCHSINE I (Gr-E)**

Color Index, 677.

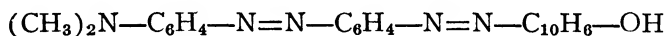


This dye is known by many synonyms. (See Color Index.) It is a triphenylmethane dye.

The dye dissolves in hot water with a red color. It also dissolves in alcohol with a red solution, but it is insoluble in ether.

**ICE BLACK**

Color Index, 265.



The dye actually is formed by coupling any of several diazotized amines with  $\beta$ -naphthol to give molecules similar to that shown above, and it appears probable that perhaps the amine is sometimes referred to as ice black.

**INDIGOSOL O4B**

Synonym: Indigosol is the sodium salt of the disulfuric ether of leucoindigo MLB/4B

**Detection of nitrite.** Migray<sup>1,2</sup> has used the dye indigosol O4B (Color Index, 1184) for the detection of small quantities of nitrite.

**Procedure.** Add 5 drops of 10 per cent indigosol and 5 ml. of 7 N sulfuric acid to 100 ml. of the solution to be tested. A dark blue color develops if the solution contains only 1.0 mg. of  $\text{N}_2\text{O}_3$  per liter of solution. A color appears

slowly with less  $\text{N}_2\text{O}_3$ , and with higher concentration of nitrite a blue precipitate forms.

1. E. v. Migray, *Chem.-Ztg.* **57**, 94 (1933); *C.A.* **27**, 1592 (1933).
2. W. Fischbach, *Z. anal. Chem.* **96**, 443-7 (1934).

### JET BLACK R(By)

$\text{C}_{32}\text{H}_{21}\text{N}_5\text{O}_6\text{S}_2\text{Na}_2$

Color Index, 296.

The dye occurs as black powder. Its aqueous solution is bluish-violet in color, and its alcoholic solution is violet. The dye also dissolves in sulfuric acid with a blue solution.

**Preparation:** Diazotize 2.33 g. of anilinedisulfonic acid and add a solution of 2 g. of  $\alpha$ -naphthylamine in hydrochloric acid. Diazotize the clear red solution with a solution of 1 g. of sodium nitrite in 10 ml. of water. Let stand several hours and filter. Add the crystals to an alcoholic solution of 3.5 g. of phenyl- $\alpha$ -naphthylamine. Let stand 24 hours, then warm gently, filter, and convert to the sodium salt.

### MAGDALA RED

Synonym: Sudan red

Magdala red (Color Index, 857), is a mixture of aminonaphthyldinaphthazonium chloride and diaminonaphthyldinaphthazonium chloride.

Magdala red consists of a dark brown powder, or is obtained as green needles by crystallizing from alcohol. It is sparingly soluble in hot water, but dissolves in alcohol to form a red solution with an orange fluorescence.

**Preparation:** Magdala red is prepared by heating  $\alpha$ -aminoazonaphthalene hydrochloride or acetate with  $\alpha$ -naphthylamine. Magdala red is formed to the extent of only 6-8 per cent in the reaction mixture, but is obtained by repeated extractions with boiling water. It is finally purified by crystallizing from water.<sup>1-3</sup>

**Detection of nitrites.** A solution of magdala red is yellow in 2 N mineral acid, pink in N mineral acid and red with a reddish fluorescence at  $\text{pH} = 4$ . It has a lilac color at  $\text{pH} = 15$ . By treating the dye with a hot solution of a nitrite it is converted into a nonfluorescent compound. This reaction has been used as the basis for a sensitive test for nitrite.<sup>4,5</sup>

**Reagent.** Dissolve 0.1 g. of magdala red in 100 ml. of water and a little acetic acid.

**Procedure.** Add a very small drop of the dye solution to 5-10 ml. of water, and add hydrochloric acid to the cold solution until the fluorescence disappears and a violet color is formed. An intense yellow-red fluorescence should appear on heating and if it does not, dilute with a little water. To this solution add a neutral or slightly alkaline solution to be tested. If nitrite is present, the fluorescence disappears immediately and a blue color forms.

The test appears to be more sensitive in the presence of cupric and ferrous ions. Nitrate does not cause a loss of fluorescence, even after long boiling. The method is particularly useful for detecting nitrite in the presence of nitrate. Sulfite, thiosulfate, hypochlorite, dichromate and permanganate interfere.

1. A. W. Hofmann, *Ber.* **2**, 374, 412 (1869).
2. O. Fischer and Hepp, *Ber.* **26**, 2235 (1893).
3. O. Fischer and Hepp, *Ann.* **286**, 235 (1895).
4. H. Eichler, *Z. anal. Chem.* **96**, 99-100 (1934); *C.A.* **28**, 2297 (1934).
5. H. Eichler, *Z. anal. Chem.* **100**, 183-90 (1935); *C.A.* **29**, 3259 (1935).

### METHYLENE HELIOTROPE OL(M)

Methylene heliotrope OL(M) consists of a mixture of basic azine dyes similar to rosolane<sup>+</sup> (Color Index, 845).

### NAKO DYES

Nako brown D is a mixture of *p*-phenylenediamine and toluenylenediamine. Other Nako colors contain *p*-aminophenol (Color Index, 875).

### NAPHTHAMINE BLACK CE

Same as direct black.

### NAPHTHOL BLUE BLACK

Same as Agalma Black 10B(B).

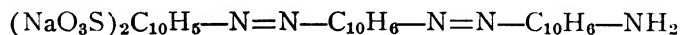
### NAPHTHYLAMINE BLACK 10B

Same as Agalma Black 10B (B).

### NAPHTHYLAMINE BLACK D

Naphthylamine black D consists of a number of compounds such as the following:

$C_{30}H_{19}N_5O_6S_2Na_2$  Color Index, 308.



The dye is a black powder, insoluble in alcohol, but soluble in water with a violet-black solution.

**NEUTRAL RED EXTRA (Kb)** Synonym: Toluylene red, neutral red

$C_{15}H_{17}N_4Cl$  Mol. Wt. 388.75 Color Index, 825.

**Use:** Detection and determination of nitrite.

The dye is a blackish-green powder, but the base forms as orange crystals. The

aqueous solution of the dye is crimson red, and the alcoholic solution is magenta-red in color with a faint brownish-red fluorescence.

**Preparation:** Neutral red extra is an azine dye prepared by the action of *p*-nitrosodimethylaniline hydrochloride on *m*-toluylenediamine, followed by the oxidation of the resulting indamine.

**Detection of nitrite.** Rochaix<sup>1,2</sup> has used neutral red as a reagent for the detection of nitrite in water.

**Reagent.** Dissolve 0.2 g. of the dye in 1 liter of water.

**Procedure.** Add 20 ml. of the reagent and 1-3 ml. of 20 per cent sulfuric acid to 10 ml. of the water to be tested. A violet to blue color appears if nitrite is present. The sensitivity of the reaction is 0.05 mg. nitrous acid per liter.

Zlataroff<sup>3,8</sup> has used a similar method, adding 1-2 ml. of 0.002-0.003 per cent neutral red solution and 2-3 ml. of dilute sulfuric acid to 10 ml. of the water to be tested. Stoof<sup>4</sup> has modified the Zlataroff procedure by using 4 ml. of 25 per cent phosphoric acid instead of the sulfuric acid. The sensitiveness of this reaction is 0.2 mg.  $N_2O_3$  per liter. Van Urk<sup>5</sup> prepared a nitrite reagent by triturating 2 g. of neutral red with 18 ml. of water, filtering, and then adding 80 g. of concentrated sulfuric acid to the cold filtrate. To test for nitrite, add 5 drops of this solution to 100 ml. of the water to be tested. The sensitiveness of this reaction is 0.1-0.2 mg. per liter.

**Determination of nitrite.** Alekseeva and Gurvits<sup>6</sup> have used the color reaction of neutral red with acid solutions of nitrites as a means of determining the latter. The reagent is prepared by mixing 666 ml. of 0.003 per cent neutral red solution with 266 ml. of 1:5 sulfuric acid and 68 ml. of water. Safranin may be used in place of the neutral red in this reaction.

1. A. Rochaix, *Compt. rend. soc. biol.* **66**, 171; *C.A.* **3**, 1133 (1909).
2. A. Rochaix, *Repert. de pharm.* 139 (1909).
3. A. Zlataroff, *Z. anal. Chem.* **384** (1923).
4. H. Stoof, *Z. anal. Chem.* **64**, 272 (1924).
5. H. W. Van Urk, *Pharm. Weekblad.* **66**, 429 (1929).
6. M. V. Alekseeva and S. S. Gurvits, *Hig. Truda.* **15**, No. 2, 65-96 (1937); *Chimie et industrie.* **39**, 474; *C.A.* **32**, 4467 (1938).
7. S. Vergnoux, *Bull. sci. pharmacol.* **36**, 146 (1929).
8. A. Zlataroff, *Grundriss der Nahrungsmittelchemie* (1921).
9. H. Storff and M. Horn, *Wasser u. Gas.* **14**, 175 (1924); *C.A.* **18**, 873 (1924).

## NEW FUCHSIN O(Gr.-E)

Synonym: New magenta

$C_{22}H_{24}N_3Cl$

Color Index, 678.

New Fuchsin is the hydrochloride of triaminotritolylcarbinol anhydride, or diaminotrimethylfuchsonimonium chloride.

The dye consists of a beetle-green powder, which dissolves in water and alcohol to form red solutions.



**NIGHT BLUE** $C_{38}H_{42}N_3Cl$ 

Color Index, 731.

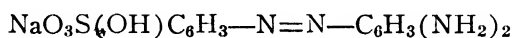
This dye is a violet powder with a bronze luster. It dissolves in water with a bluish-violet solution. It also dissolves readily in alcohol with a violet color.

**OXAMINE BLACK BHN**

Same as direct black.

**PALATINE CHROME BROWN W** $C_{12}H_{11}N_4O_4SNa$ 

Color Index, 167.

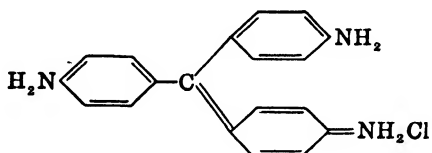


Palatine chrome brown W is an azo dye prepared by coupling diazotized *o*-aminophenol-*p*-sulfonic acid with *m*-phenylenediamine.

The dye is a black-brown powder with a greenish appearance. It dissolves in hot water with a brown solution. It is also soluble in hydrochloric acid with a reddish-yellow solution, and in sodium hydroxide with a redder solution.

**PARAROSANILINE BASE** $C_{19}H_{18}N_3Cl \cdot 4H_2O$ 

Color Index, 676.



The dye occurs as glistening crystals. It is sparingly soluble in water, but is readily soluble in alcohol with a crimson solution. Its sulfuric solution is yellow.

**PHOSPHINE E**

Synonym: Phosphine N(B), phosphine O(M), phosphine 3R(K), phosphine NA(K), phosphine P(K)

Phosphine E (Color Index, 793) is a mixture of the nitrates of chrysaniline. It is a by-product of the manufacture of magenta. It is an orange-yellow powder. It dissolves in water to form a reddish-yellow solution with a green fluorescence.

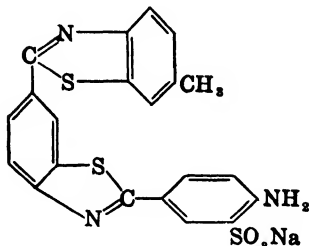
**POIRRIER BLUE C4B**

Poirrier Blue C4B is the sodium or potassium salt of triphenylrosaniline-sulfonate. It is soluble in water and alcohol. The aqueous solution at pH 11.0 is blue, and at pH 13.0 a violet red.

**PRIMULINE**

Color Index, 812.

Primuline is not a pure compound, but consists essentially of the following thiazole derivative:



The dye is a dull yellow powder. It dissolves in water to form a pale yellow solution with a blue fluorescence at great dilution.

**Preparation:** See page 391.<sup>1</sup>

1. Gattermann, *Ber.* 22, 422 (1889).

**PURE BLUE BSJ**
 $C_{37}H_{27}N_3O_9S_3Na_2$ 

Color Index, 706.

This dye is a dark blue powder. It dissolves in water with a blue solution, and in sodium hydroxide and in sulfuric acid with reddish-brown solutions.

**RED VIOLET 4RS(B)**

Same as Acid Violet 4RS.

**RHEONIN A**

Synonym: Rheonin AL, Rheonin N

 $C_{23}H_{25}N_4Cl$ 

Color Index, 795.

Rheonin A is an acridine dye.

Rheonin A is a brown powder. It dissolves in water, alcohol, and sulfuric acid with the formation of brownish-yellow solutions with a green fluorescence. Rheonin N is of a somewhat brighter shade.

The dye is prepared according to the method of Grandmougin and Lang.<sup>1</sup>

1. Grandmougin and Lang, *Ber.* 42, 3634 (1909).

**RHODAMIN 3G EXTRA**
 $C_{25}H_{25}N_2O_3Cl$ 

Color Index, 753.

Rhodamin 3G extra is a xanthine dye.

The dye occurs as a green crystalline powder. It is soluble in water, forming a crimson-red solution with a brown fluorescence. It also dissolves in alcohol

to form a scarlet-red solution with a green fluorescence. Its sulfuric acid solution is yellow.

### RHODULIN RED B(By)

Rhodulin red B(By) (Color Index, 844) is a mixture of azine dyes obtained by the action of *p*-nitrosodimethylaniline hydrochloride on phenyl- (or *p*-tolyl)-*p*-amino-*o*-toluidine. It occurs as a brown powder. In character it is somewhat similar to rhodulin violet.

### RHODULIN VIOLET (By)

Rhodulin violet (By) (Color Index: 844) is an azine dye prepared by the action of *p*-nitrosodimethylaniline hydrochloride on phenyl- (or *p*-tolyl) *p*-amino-*o*-toluidine, or on *sym*-phenyl- (or *p*-tolyl)-*p*-aminobenzyl-*o*-toluidine.

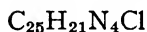
The dye is a glistening black-green powder. It dissolves in water to form a red solution, and in alcohol to form a solution with a red to brown fluorescence. Its sulfuric acid solution is green.

### ROSANTHRENE VIOLET 5R

Rosanthere violet 5R is an azo dye which is used for diazotization and development with  $\alpha$ -naphthol.

### ROSOLANE O

Synonym: Methyl heliotrope

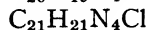


Color Index, 845.

This azine dye is prepared by the oxidation of a mixture of *p*-aminodiphenylamine, aniline, and *o*-toluidine.

The dye is a greenish-olive powder. It is sparingly soluble in water with a red-violet color. It is also sparingly soluble in alcohol, but dissolves in sulfuric acid with a green solution.

### SAFRANINE



Color Index, 841.

The dye is a reddish-brown powder, soluble in water with a red solution, and in alcohol with a red solution possessing a yellowish fluorescence. The sulfuric acid solution is green. The dye may be prepared according to the method of Perkin.<sup>1</sup>

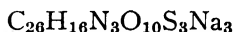
1. Perkin, *J. Chem. Soc.* 14, 235 (1862).

### SPIRIT YELLOW

Same as *p*-aminoazobenzene.

**SULFON ACID BLUE G**

This dye belongs to the same class as sulfon acid blue R.

**SULFON ACID BLUE R**

Color Index, 208.

The dye occurs as a black powder with a reddish tint. It dissolves in water with a reddish-violet solution. It also dissolves in hydrochloric acid with a greenish-blue solution, and in sodium hydroxide with a bright red solution.

**SULFON BLACK R(By)**

Color Index, 271.

Sulfon black R(By) is an azo dye.

This dye may be prepared according to a method described in *Chem. Ind.* **19**, 548 (1896). It is a dark brown powder. It dissolves in water sparingly with the formation of a reddish-violet solution.

**SULFON CYANINE**

Same as Cloth Fast blue.

**SULFON CYANINE BLACK B AND 2B**

Same as Cloth Fast Black.

**TANNIN HELIOTROPE**

Tannin heliotrope (Color Index, 852) is an azine dye prepared by the action of *p*-nitrosodimethylaniline hydrochloride on a mixture of the hydrochlorides of *m*- and *p*-xylydines.

The dye occurs as a brown paste or a greyish-green powder, which dissolves in water and alcohol with the formation of magenta-red solutions. Its sulfuric acid solution is green.

**TOLYL BLACK B**

Same as Cloth Fast Black.

**TOLYL BLACK BB(M)**

Same as Cloth Fast Black.

**TOLYL BLUE GR EXTRA**

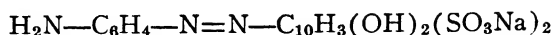
Similar to Cloth Fast Blue.

**TOLYL BLUE 5R EXTRA**

Same as Cloth Fast Blue.

**VICTORIA VIOLET 4BS**

Color Index, 53.



The compound is a gray-green powder. It dissolves in water to form a dark violet solution, and in sulfuric acid to form a bluish-red solution. It is difficultly soluble in alcohol.

**Preparation:** Chromotrope 2B, obtained from 138 parts of *p*-nitroaniline and 400 parts of chromotropic acid, is dissolved in 15-20 times its weight of warm water, and to this is added a 20 per cent solution of sodium sulfide until a test does not become bluer with more sodium sulfide. Neutralize with dilute acid and salt out.

**WATER BLUE 3B(K)**

Water Blue 3B(K) (Color Index, 707) is a triphenylmethane dye. It occurs as a blue powder or lumps, or as coppery flakes. It dissolves in water with a blue solution, but it is almost insoluble in alcohol.

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 thiocarbonyl, 158  
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 sodium diethyldithiocarbamate, 91  
 tetramethyl-p-diaminodiphenylmethane,  
     562  
 thionalide, 171  
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**Detection of Lithium**

alizarinsulfonic acid, 433  
 1-amino-4-hydroxyanthraquinone, 442  
 methyl orange, 532

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 aniline yellow S, 473  
 azo blue, 337  
 benzoazurine G, 337  
 benzopurpurin 4B, 338  
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 Chicago blue 6B(A), 347  
 congo corinth, 348  
 diamine pure blue FF(C), 349  
 diamond black F, 484  
 gallocyanine, 361  
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 p-nitrobenzeneazoresorcinol, 381  
 p-nitrodiazoaminoazobenzene, 343  
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 resorufin, 390  
 2,4,5,7-tetranitro-1,8-dihydroxyanthra-  
     quinone (sodium salt), 471  
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**Determination of Magnesium**

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 dextrin, 280  
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 gum arabic, 304  
 methylene blue, 525  
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quinalizarin, 457  
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 strychnine, 272  
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 gallocyanine, 361  
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 sodium diethyldithiocarbamate, 91  
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**Determination of Manganese**

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 brilliant violet, 342  
 bromophenol blue, 478  
 brucine, 213  
 cacotheline, 220  
 cellulose, 279  
 dipicrylamine, 10  
 erythrosin, 360  
 fluorescein, 494  
 gallocyanine, 361  
 Hoffman violet 3R, 369  
 2-mercaptobenzimidazole, 127  
 mercaptophenylthiodiazolone, 129  
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 methyl orange, 532  
 naphthol yellow S, 19  
 narcotine, 249  
 phenosafranine, 385  
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**Detection of Mercury (Continued)**

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 picric acid, 35  
 picrolonic acid, 45  
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 1-(2-quinolyl)-4-allylthiosemicarbazide, 148  
 rhodamine B, 556  
 sodium diethyldithiocarbamate, 91  
 starch, 286  
 strychnine, 271  
 thiocarbene, 158  
 thiourea, 178  
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**Determination of Mercury**

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 2-mercaptobenzimidazole, 127  
 phenylthiohydantoic acid, 139  
 starch, 286  
 strychnine, 271  
 tetraphenylarsonium chloride, 326  
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 cinchonine, 233  
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 tetramethyl-p-diaminodiphenylmethane, 566  
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 toluene-3,4-dithiol, 193  
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**Determination of Molybdenum**

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 methylene blue, 520  
 potassium xanthate, 103  
 thioacetic acid, 157  
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**Detection of Neodymium**

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**Detection of Nickel**

alkannin, 336  
 ammonium dithiocarbamate, 77  
 aniline yellow S, 473  
 benzo fast yellow 5 GL, 477  
 2-benzothiazolethiol, 111  
 brilliant yellow, 342  
 cellulose, 279  
 congo corinth, 348  
 cyclohexylethylaminedithiocarbamate, 79  
 1,2-diaminoanthraquinone-3-sulfonic acid, 350  
 diamond black F, 484  
 gallocyanine, 361  
 mercaptophenylthiothiodiazolone, 129  
 methyl orange, 532  
 p-nitrobenzeneazoresorcinol, 382  
 phenylthiosemicarbazide, 140  
 potassium dithiooxalate, 143  
 picric acid, 35  
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 potassium thiocarbonate, 146  
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 1-(2-quinolyl)-4-allylthiosemicarbazide, 148  
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**Determination of Nickel**

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 oxanilic acid thioamide, 135  
 potassium dithiooxalate, 143  
 potassium thiocarbonate, 146  
 potassium xanthate, 104  
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 arbutin, 294  
 azorubine, 476  
 berberine, 207  
 brucine, 207  
 cinchonamine, 224  
 di-(9,10-monohydroxyphenanthryl)amine, 485  
 $\beta$ -naphthylimino-8-dinaphthoxazine, 538  
 narcotine, 249  
 phenylimino-8-dinaphthoxazine, 548  
 rubrophen, 558  
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**Determination of Nitric Acid**

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**Determination of Nitric Acid (Continued)**

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 azorubine, 476  
 benzocyanine B, 580, 586  
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 benzo red blue G, 581, 586  
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 Chicago blue B, 580, 586  
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 cloth fast black B, 582, 588  
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 starch, 285  
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**Determination of Nitrite**

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 fuchsin, 500  
 neutral red extra (Kb), 593  
 novocaine, 250  
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**Detection of Osmium**

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 caffeine, 224  
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**Detection of Osmium (Continued)**

cocaine, 238  
 ephedrine, 243  
 espartine, 244  
 phenolphthalin, 545  
 picramic acid, 38  
 potassium thiocarbonate, 147  
 quinidine sulfate, 251  
 quinine, 254  
 strychnine, 272  
 thiocarbamilide, 157  
 thiourea, 178, 183

**Determination of Osmium**

strychnine, 272  
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**Detection of Oxidizing Agents**

acetanilide, 313  
 apomorphine, 205  
 codeine, 241  
 phenolphthalin, 545  
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**Determination of Oxidizing Agents**

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**Detection of Oxygen**

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**Determination of Oxygen**

caramel, 296  
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**Detection of Ozone**

fluorescein, 492  
 indigo carmine, 510  
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 tetramethyl-p-diaminodiphenylmethane, 567

**Determination of Ozone**

fluorescein, 492  
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**Detection of Palladium**

brucine, 216  
 caffeine, 223  
 cinchonidine, 225  
 cinchophen, 236

cocaine, 238  
 espartine, 244  
 2-mercaptobenzimidazole, 127, 128  
 methyl orange, 532  
 $\alpha$ -nitro- $\beta$ -naphthol, 24  
 phenylthiourea, 141  
 quinidine sulfate, 251  
 quinine, 254  
 rubeanic acid, 154  
 starch, 286  
 strychnine, 272  
 thiocarbamine, 158  
 thiourea, 178, 185

**Determination of Palladium**

2-mercaptobenzimidazole, 127  
 $\alpha$ -nitro- $\beta$ -naphthol, 24  
 sodium diethyldithiocarbamate, 90  
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**Detection of Perchlorate**

brucine, 215  
 methylene blue, 521  
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**Determination of Perchlorate**

methylene blue, 521  
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**Detection of Periodate**

tetramethyl-p-diaminodiphenylmethane, 566

**Determination of Periodate**

tetraphenylarsonium chloride, 326

**Detection of Permanganate**

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**Determination of Permanganate**

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**Detection of Persulfate**

brucine, 215  
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**Determination of Persulfate**

brucine, 215

**Detection of Phosphorus**

gelatin, 299  
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 quinine, 254  
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**Determination of Phosphorus**

methylene blue, 520  
 quinalizarin, 457  
 quinine, 254  
 strychnine, 261

**Detection of Platinum**

alizarin, 411  
 alizarinsulfonic acid, 433  
 brucine, 216  
 cinchonidine, 225  
 cinchophen, 236  
 cocaine, 238, 239  
 cochineal, 446  
 cystine, 122  
 espartine, 244  
 $\alpha$ -naphthoflavone, 323  
 narcotine, 249  
 phenylthiosemicarbazide, 140  
 phenylthiourea, 141  
 quinidine sulfate, 251  
 quinine, 254  
 rubeanic acid, 154  
 starch, 286  
 strychnine, 272  
 thiourea, 178, 185

**Determination of Platinum**

sodium diethyldithiocarbamate, 89

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alizarinsulfonic acid, 433  
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 6-chloro-5-nitrotoluene-3-sulfonic acid, 2  
 1,5-dinitro-2-naphthol-7-sulfonic acid, 6  
 2,4-dinitrophenol, 7  
 2,6-dinitrophenol, 7  
 dipicrylamine, 9, 10  
 hymolal, 305  
 lokaonic acid, 306  
 naphthalene- $\alpha$ -sulfonic acid, 198  
 naphthol yellow S, 19  
 nitranilic acid, 21  
 5-nitrobarbituric acid, 22  
 p-nitrophenol, 26  
 oil of clove, 306  
 picric acid, 27, 35  
 picrolonic acid, 45  
 2,4,6-trinitro-m-cresol, 47  
 2,4,6-trinitroresorcinol, 47

**Determination of Potassium**

6-chloro-5-nitrotoluene-3-sulfonic acid, 2  
 cysteine, 120  
 dipicrylamine, 10, 14  
 2-hydroxynaphthalene-1-azo-naphthalene-4-sulfonic acid, 504  
 methylene blue, 525  
 naphthalene- $\alpha$ -sulfonic acid, 198  
 naphthol yellow S, 19  
 5-nitrobarbituric acid, 22  
 picric acid, 28

**Detection of Praseodymium**

methyl orange, 532  
 morphine, 247  
 quinalizarin, 466

**Detection and Determination of Rare Earths**

2-(o-arsonophenylazo)-p-cresol, 74  
 1-(o-arsonophenylazo)-2-naphthol-3,6-disulfonic acid, 74  
 1-(o-arsonophenylazo)-2-naphthol-6,8-disulfonic acid, 74  
 3-(o-arsonophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulfonic acid, 74  
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**Detection of Rhenium**

brucine, 215  
 cacotheline, 220  
 methylene blue, 525  
 potassium xanthate, 106  
 strychnine, 272  
 toluene-3,4-dithiol, 193  
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**Determination of Rhenium**

tetraphenylarsonium chloride, 329

**Detection of Rhodium**

brucine, 216  
 cacotheline, 219  
 cinchophen, 236  
 quinidine sulfate, 251  
 strychnine, 272  
 thiourea, 185

**Determination of Rhodium**

thionalide, 175

**Detection of Rubidium**

6-chloro-5-nitrotoluene-3-sulfonic acid, 4  
 1,5-dinitro-2-naphthol-7-sulfonic acid, 6

**Detection of Rubidium (Continued)**

2,4-dinitrophenol, 7  
 dipicrylamine, 10  
 methyl orange, 532  
 naphthol yellow S, 20

**Determination of Rubidium**

6-chloro-5-nitrotoluene-3-sulfonic acid, 4  
 dipicrylamine, 10

**Detection of Ruthenium**

brucine, 216  
 cinchophen, 236  
 cocaine, 238  
 rubeanic acid, 154  
 strychnine, 272  
 substituted thioureas, 190  
 thiobromine, 274  
 thiocarbamilide, 157  
 thiourea, 178, 184, 185

**Determination of Ruthenium**

phenylthiosemicarbazide, 141  
 thioanilide, 175  
 thiourea, 184

**Detection of Scandium**

alizarin, 411  
 alizarinsulfonic acid, 433  
 o-aminobenzeneearsonic acid, 51  
 cochineal, 446  
 morin, 374  
 quinalizarin, 465

**Determination of Scandium**

morin, 374

**Detection of Selenium**

aspidospermine, 206  
 codeine, 239  
 colchicine, 242  
 $\alpha$ -naphthoflavone, 323  
 quinine, 254  
 thiourea, 178, 185  
 veratrine, 275

**Determination of Selenium**

codeine, 240  
 gum arabic, 304

**Detection of Silicon**

cocaine, 237  
 coniine, 242  
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**Determination of Silicon**

agar, 292  
 albumin, 293  
 casein, 296  
 cocaine, 237  
 gelatin, 298  
 picric acid, 32

**Detection of Silver**

ammonium dithiocarbamate, 77  
 benzopurpurin, 4B, 339  
 brilliant violet, 342  
 cellulose, 280  
 cinchophen, 236  
 dextrin, 280  
 fluorescein, 494  
 gallocyanine, 361  
 glucose, 282  
 2-mercaptobenzimidazole, 127  
 mercaptophenylthiothiodiazolone, 129  
 methylene blue, 523  
 methyl orange, 532  
 phenosafranin, 385  
 phenylthiohydantoic acid, 139  
 phenylthiourea, 141  
 picric acid, 35  
 ponceau 2R, 386  
 pyronin, 388  
 1-(2-quinolyl)-4-allylthiosemicarbazide, 148  
 resorufin, 390  
 starch, 286  
 sucrose, 290  
 thiocarbamine, 158  
 thiourea, 178

**Determination of Silver**

albumin, 292  
 dextrin, 280  
 gelatin, 299  
 gum arabic, 304  
 2-mercaptobenzimidazole, 127  
 phenylthiohydantoic acid, 139  
 starch, 286  
 sucrose, 290  
 thionalide, 170, 175

**Detection of Sodium**

2,6-dinitrophenol, 7  
 nitranilic acid, 21  
 picric acid, 34, 35  
 picrolonic acid, 45

**Determination of Sodium**

alizarin, 415

**Detection of Strontium**

alizarinsulfonic acid, 433  
 diamond black F, 484  
 methyl orange, 532  
 morin, 376  
 picric acid, 35  
 picrolonic acid, 40  
 resorufin, 390  
 2,4,5,7-tetranitro-1,8-dihydroxyanthraquinone (sodium salt), 471

**Determination of Strontium**

diamond black F, 484

**Detection of Sulfate**

phenolphthalein, 542

**Determination of Sulfate**

agar, 292  
 gelatin, 299

**Detection of Sulfide**

nitrobenzene, 23  
 quinine, 258

**Detection of Sulfite**

fast blue R, 487  
 fuchsin, 500  
 malachite green, 516  
 quinine, 258

**Determination of Sulfite**

fuchsin, 500

**Detection of Tantalum**

benzenearsonic acid, 56  
 brilliant green, 341  
 methylene blue, 525  
 methyl violet, 538  
 morphine, 247  
 rhodamine B, 556

**Determination of Tantalum**

2-(o-arsonophenylazo)-p-cresol, 75  
 1-(o-arsonophenylazo)-2-naphthol-3,6-disulfonic acid, 75  
 1-(o-arsonophenylazo)-2-naphthol-6,8-disulfonic acid, 75  
 3-(o-arsonophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulfonic acid, 75  
 benzenearsonic acid, 56

**Detection of Tellurium**

$\alpha$ -naphthoflavone, 323  
 potassium methylxanthate, 96  
 potassium xanthate, 105

quinine, 254  
 thiourea, 186

**Detection of Thallium**

alizarin, 411  
 alizarinsulfonic acid, 433, 434  
 2-benzothiazolethiol, 112  
 cochineal, 446  
 2,4-dinitro-1-naphthol, 5  
 2,4-dinitrophenol, 7  
 dipicrylamine, 10  
 leuco-nitro diamond green, 512  
 picric acid, 34, 35  
 potassium thiocarbonate, 147  
 quinalizarin, 466  
 rhodamine B, 555  
 thiourea, 178  
 2,4,6-trinitroresorcinol, 47

**Determination of Thallium**

2-benzothiazolethiol, 113  
 chloramine T, 319  
 thionalide, 173, 175  
 thiourea, 183

**Determination of Thiocyanate**

chloramine T, 317

**Detection of Thorium**

alizarin, 416  
 alizarinsulfonic acid, 434  
 1-amino-4-hydroxyanthraquinone, 442  
 2-(o-arsonophenylazo)-p-cresol, 75  
 1-(o-arsonophenylazo)-2-naphthol-3,6-disulfonic acid, 75  
 1-(o-arsonophenylazo)-2-naphthol-6,8-disulfonic acid, 75  
 3-(o-arsonophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulfonic acid, 75  
 benzenesulfonic acid, 202  
 cochineal, 447  
 methyl orange, 532  
 morin, 375  
 quinalizarin, 466

**Determination of Thorium**

benzenearsonic acid, 55  
 benzenesulfonic acid, 202  
 $\alpha$ -naphthalenesulfonic acid, 203  
 $\beta$ -naphthalenesulfonic acid, 203  
 picrolonic acid, 44

**Detection of Tin**

alizarinsulfonic acid, 433  
 ammonium dithiocarbamate, 77  
 anthragallol, 439  
 anthraquinone-1-azo-4-dimethylaniline, 474

**Detection of Tin (Continued)**

anthrapurpurin, 440  
 2-(o-arsonophenylazo)-p-cresol, 75  
 1-(o-arsonophenylazo)-2-naphthol-3,6-disulfonic acid, 75  
 1-(o-arsonophenylazo)-2-naphthol-6,8-disulfonic acid, 75  
 3-(o-arsonophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulfonic acid, 75  
 benzenearsonic acid, 54  
 benzenesulfonic acid, 202  
 brilliant violet, 342  
 brucine, 213  
 cacotheline, 218  
 cerulein, 479  
 4-chloro-1,2-dimercaptobenzene, 116  
 diazin green S(K), 485  
 flavopurpurin, 448  
 gallocyanine, 361  
 glucose, 282  
 hematein, 364  
 hematoxylin, 366  
 Hoffman violet 3R, 369  
 methylene blue, 523  
 methyl orange, 532  
 naphthol yellow S, 19  
 m-nitrophenylarsonic acid, 72  
 pyronin, 388  
 quinalizarin, 467  
 quinine, 253  
 rufigallic acid, 470  
 thioglycolic acid, 162  
 toluene-3,4-dithiol, 191

**Determination of Tin**

agar, 292  
 anthraquinone-1-azo-4-dimethylaniline, 474  
 benzenesulfonic acid, 202  
 cacotheline, 219  
 chloramine T, 317, 319  
 4-chloro-1,2-dimercaptobenzene, 116, 117  
 dinitrodiphenylaminesulfoxide, 197  
 hematoxylin, 368  
 methylene blue, 519  
 methyl orange, 532  
 $\alpha$ -naphthalenesulfonic acid, 203  
 $\beta$ -naphthalenesulfonic acid, 203  
 tetraphenylarsonium chloride, 327  
 thionalide, 175  
 thionine, 570  
 toluene-3,4-dithiol, 192

**Detection of Titanium**

alizarin, 416  
 alizarinsulfonic acid, 433  
 apomorphine, 205

2-(o-arsonophenylazo)-p-cresol, 75  
 1-(o-arsonophenylazo)-2-naphthol-3,6-disulfonic acid, 75  
 1-(o-arsonophenylazo)-2-naphthol-6,8-disulfonic acid, 75  
 3-(o-arsonophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulfonic acid, 75  
 benzenesulfonic acid, 202  
 brucine, 215  
 cacotheline, 219  
 cerulein, 479  
 indigo carmine, 510  
 methylene blue, 518  
 morphine, 247  
 narcotine, 250  
 turmeric, 405

**Determination of Titanium**

benzenesulfonic acid, 202  
 Congo red, 482  
 p-hydroxyphenylarsonic acid, 66, 67  
 methylene blue, 518  
 methyl orange, 533  
 picric acid, 33  
 thioglycolic acid, 162

**Detection of Tungsten**

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**Determination of Tungsten**

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**Determination of Uranium**

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**Determination of Water**

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p-nitrobenzeneazoresorcinol, 382  
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 1-(o-arsonophenylazo)-2-naphthol-6,8-disulfonic acid, 75  
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**Detection of Zirconium**

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**Determination of Zirconium**

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